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COLLABORATIVE TEST OF THE CHEMILUMINESCENT METHOD
FOR MEASUREMENT OF NO₂ IN AMBIENT AIR

Paul G. Constant, Jr., et al

Midwest Research Institute

Prepared for:

National Environmental Research Center

February 1975

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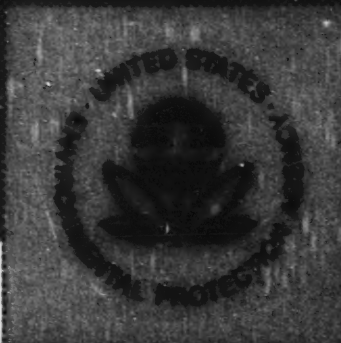
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**COLLABORATIVE TEST
OF THE CHEMILUMINESCENT METHOD
FOR MEASUREMENT OF NO₂
IN AMBIENT AIR**

by

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Prepared for
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WASHINGTON, D. C. 20460

February 1975

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FOREWORD

This program, "Collaborative Testing of Methods for Measurement of NO₂ in Ambient Air," is being conducted under the Environmental Protection Agency Contract No. 68-02-1363, which is Midwest Research Institute's Project No. 3823-C. The program is concerned with the evaluation of the following four methods with regard to their precision and accuracy:

1. Sodium-Arsenite,
2. TGS-ANSA,
3. Continuous-Colorimetric, and
4. Chemiluminescent.

The collaborative study covered by this report is of the Chemiluminescent Procedure, which is a tentative instrumental method. In summary, MRI's responsibility was to develop an NO₂, ambient-air sampling system for use with the four methods, provide the test site and facilities thereon where the collaborative tests would be conducted, select the collaborators with regard to the program, prepare a plan of test for the collaborative test, schedule testing, coordinate the test, retrieve field data and results from the collaborators, statistically analyze their results, and report its findings to EPA. The 10 collaborators who participated in the chemiluminescent collaborative test are:

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This report of test summarizes MRI's and the collaborators' activities. It describes the development of the NO₂ ambient-air sampling system, which covers the general concept of the system, design considerations, the design of the system and the system checkout. Following this, there are discussions on the test site, the selection of collaborators, the formal statistical design including the presentation of factors and parameters that were considered, the collaborators' field sampling at the test site, the collaborators' analysis results, MRI's statistical analyses of the collaborators' results, conclusions, and recommendations. Appendices contain a copy of the tentative Chemiluminescent Method, information on the permeation tubes prepared for this program by the National Bureau of Standards, written communiques with collaborators, instructions for collaborators, and MRI's field, operational, and data log sheets.

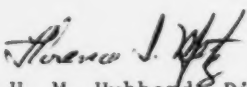
Those individuals named above with the collaborating organizations are acknowledged for their excellent work in the chemiluminescent collaborative test.

Special acknowledgements are made to the National Bureau of Standards and to Mr. Ernest E. Hughes and Dr. John K. Taylor of NBS who provided the NO₂ permeation tubes for this collaborative test; and to Dr. John B. Clements, Chief, Methods Standardization and Performance Evaluation Branch, National Environmental Research Center, Environmental Protection Agency, and Mr. John H. Margeson, Government Project Officer, Methods Standardization and Performance Evaluation Branch for their valuable suggestions in planning and design.

This MRI collaborative program was conducted under the management and technical supervision of Mr. Paul C. Constant, Jr., Head, Environmental Measurements Section of MRI's Physical Sciences Division, who was the program manager. Those who contributed to this test are: development of the NO₂ ambient-air sampling system - Dr. Chatten Cowherd, Jr., Mr. Fred Bergman, Mr. Emile Baladi, and Mr. Wallace Yocum; experimental design and statistical analysis - Mr. Michael C. Sharp; and preparation and operation of test facilities - Dr. George W. Scheil, Mr. John LaShelle, Mr. Donald Cushing, and Mr. Edward Cartwright, Jr.

Approved for:

MIDWEST RESEARCH INSTITUTE


for H. M. Hubbard, Director
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September 22, 1975

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SUMMARY

A collaborative test was conducted by Midwest Research Institute (MRI) in the Greater Kansas City Area during September 23 to 27, 1974. Ten collaborators participated in this test of the "Tentative Method for the Continuous Measurement of Nitrogen in the Atmosphere (Chemiluminescent Procedure)." All collaborators sampled from the NO₂, ambient-air sampling system that was developed by MRI specifically for this collaborative test program. For each of the four test days, a different average NO₂ challenge (spike) was used: 48.6, 102, 186, and 292 µg/m³. These levels were obtained from permeation tubes that were developed by the National Bureau of Standards (NBS).

The collaborators sampled from both the spiked and unspiked (ambient) lines of the NO₂, ambient-air sampling system, providing three sets of collaborator results per test day. The first set of data per 24-hr period (a test day) comprised results where all 10 collaborators sampled from the spiked line for approximately 14 hr (1800 to 0800). The second set of data per test day comprised results collected for approximately 3 hr and 20 min (0930 to 1250) by the collaborators who were divided into two groups of five collaborators each, with one group sampling from the spiked line while the other group sampled from the unspiked line. The third set of data per test day comprised results collected for approximately 3 hr and 40 min (1250 to 1630), with the two groups interchanging sampling lines. These 12 sets of results were used for determining the bias and precision of the collaborators' measurements.

In general, the measurement error (σ_e) is around 6% and the collaborator variability $\sqrt{\sigma_e^2 + \sigma_c^2}$ about 14% for the NO₂ concentrations examined.

These values (particularly σ_e) do depend on the NO₂ level.

The average bias is low (about -5%), and in general, stable versus NO₂ level. However, one collaborator had very large biases, and another collaborator had unstable biases (as a function of NO₂ level). Nevertheless, it is fair to say that for most collaborators (8 out of 10) using the Chemiluminescent Method, the bias is small and well balanced.

In summary then, collaborators using the Chemiluminescent Procedure produce reproducible values with little bias on the average.

Two methods of estimating the lower detectable limit (LDL) were used. From the results of these calculations, it is reasonable to state that the LDL within a collaborator is probably $\leq 13 \mu\text{g}/\text{m}^3$, and the LDL from a set of collaborators is $\leq 22 \mu\text{g}/\text{m}^3$.

The major conclusion that can be drawn from the results of this collaborative test is:

The "Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere (Chemiluminescent Procedure)" is adequately written for those knowledgeable in sampling and analysis techniques presented therein.

Based upon the conclusion that has been drawn from the results of this collaborative test, it is recommended that no further collaborative testing and analysis be done on any of the four methods tested--sodium-arsenite, TGS-ANSA, continuous colorimetric, and chemiluminescent.

INTRODUCTION

The Methods Standardization and Performance Evaluation Branch, National Environmental Research Center of the Environmental Protection Agency (EPA), is engaged in a program to evaluate four methods for measuring NO_2 in ambient air. Midwest Research Institute worked for EPA under Contract No. 68-02-1363 to provide EPA data on the precision and bias of the following four methods: sodium-arsenite and TGS-ANSA, which are manual methods, and continuous-colorimetric and chemiluminescent, which are instrumental methods.

To achieve this objective, a collaborative testing program was conducted that will assess interlaboratory as well as intralaboratory testing. In summary, MRI in the execution of this program selected the collaborators, provided sampling locations and facilities thereon, oriented the collaborators relative to the program, prepared a plan of test for each method tested, scheduled testing, coordinated the collaborative tests, retrieved field data and results of the collaborators' analyses, statistically analyzed results received from the collaborators, and reported results of the program to EPA.

This report discusses the activities performed by MRI during the fourth and final test undertaken on the contract. The method investigated was the "Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere (Chemiluminescent Procedure)," dated August 1974. A copy of the write-up of this method is given in Appendix A.

The program was initiated on June 30, 1973, and this collaborative test took place at MRI's field station in Kansas City, Missouri, during September 23 through 27, 1974, with 10 different collaborators. The interim period was devoted to the preparation for this test and conduction of the first three collaborative tests, which covered the sodium-arsenite, TGS-ANSA, and continuous colorimetric procedures. A major task of the preparation activity was the development of a precise NO_2 , ambient-air sampling system that could be housed indoors and be suitable for all four methods.

The two major phases of the test program were sampling and analysis. The sampling phase covered the field test where the collaborators obtained continuous analog NO₂ readings from the ambient-air sampling system. The analysis phase covered the calculation of average NO₂ levels from the recorder charts and the statistical analyses of their results by MRI. After the field test, the collaborators returned to their home laboratories where they analyzed their recorder charts and reported their results to MRI. Then MRI performed its statistical analysis and prepared this report of the chemiluminescent collaborative test.

This report covers the collaborative test of the tentative Chemiluminescent Method in the following order: the second section discusses the NO₂, ambient-air sampling system MRI developed for this program, covering the general concept of the system, the design considerations, the system design, and the system checkout. The third section describes the test site and the facilities that were used at this site. The fourth section discusses how the collaborators were selected and who they are. The fifth section presents the factors and parameters that were considered in the formal experimental design as well as the formal design. The sixth section summarizes the test activities during the collaborative test. The seventh section discusses the analyses that were performed by the collaborators. The collaborators' results are presented in this section along with MRI's test data. The eighth section discusses the statistical analysis of the collaborators' results and presents the results from this analysis, which includes biases and components of variance. The ninth and tenth sections present conclusions and recommendations, respectively.

The appendices contain a copy of the tentative Chemiluminescent Procedure, data on the permeation tubes that were used as the source of NO₂ in the spiked section of the sampling system, information concerning the calibration of the venturi and dry-gas meter, copies of written communiques MRI had with the collaborators, a copy of the test instructions that were given to the collaborators, the NO₂, ambient-air sampling system's operational data, results of MRI's analyses, and additional statistical analysis information.

NO₂, AMBIENT-AIR SAMPLING SYSTEM

GENERAL CONCEPT

Primary requirements for the evaluation of an ambient-air method by on-site collaborative testing are: (a) that all collaborators sample the same air; (b) that the samples be representative of ambient air; and (c) that the concentration of NO₂ in the samples be accurately known and controllable over the region of interest. The first requirement can be met by using a manifold system with each collaborator taking samples from a common stream of air. The second and third requirements are somewhat antagonistic to each other and not as easily solved.

Ideally, these requirements can be met by obtaining actual ambient samples over a wide range of concentration. However, this approach would require that each level be obtained at a different location with the additional requirement of fortuitous weather conditions, since weather conditions have a strong effect on ambient NO₂ concentrations. An additional problem with this approach is that no accepted primary reference method exists for the analysis of NO₂ in ambient air.

However, gravimetrically calibrated NO₂ permeation tubes are available which generate a stable, precise rate of release of high purity NO₂ over a period of a few years. By using a set of these tubes, different levels of NO₂ can be generated by adding the NO₂ from the permeation tubes to a stream of air of a known flow rate. Since the test conditions must relate to actual ambient air conditions, the NO₂ from the permeation tube can be added as a known addition or spike to the ambient air stream. The method under test should show a difference in concentration between samples of ambient and spiked air equal to the spike level. To ensure that the NO₂ concentration of the spiked sample does not exceed the maximum level of interest--350 µg/m³--and to allow control of the spiked air NO₂ level over a reasonably broad range, the average ambient levels must be well below the lowest NO₂ concentration to be tested, in this case, 50 µg/m³.

To achieve this, the following system is used: outdoor ambient air is drawn into the sampling system through a single tube, as shown in Figure 1. The air is divided downstream into two sections--spiked and

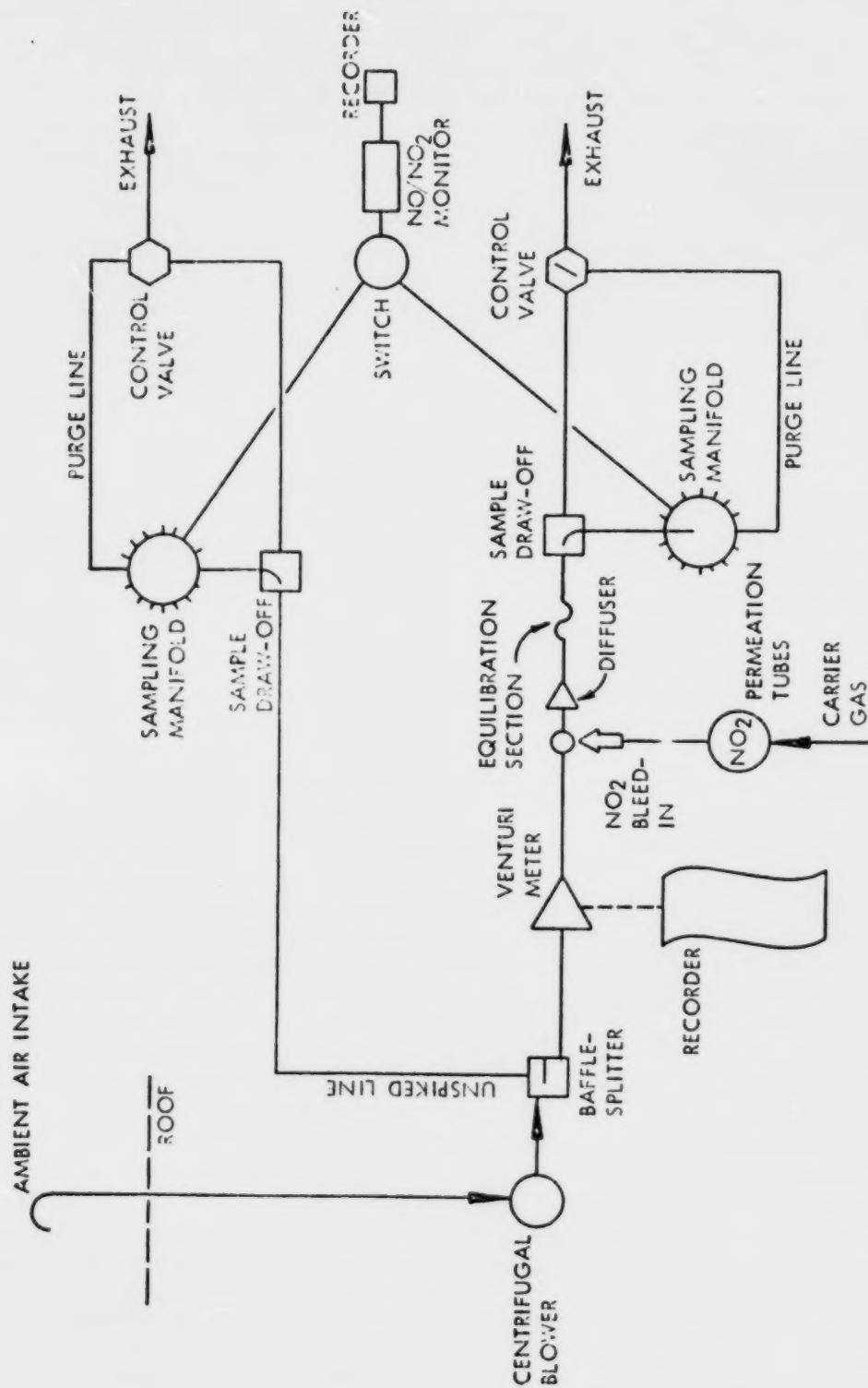


Figure 1. NO₂, ambient-air sampling system concept

unspiked. A controlled flow of ambient air at a specific value exists in the spiked section. A comparable ambient-air flow exists in the unspiked section, but the latter is uncontrolled. Temperature-controlled permeation tubes provide the source of NO_2 which is injected into the spiked section at a desired level. The NO_2 is then thoroughly mixed with the ambient air in a mixing unit--a diffuser. The mixture is then equilibrated before it reaches the sampling station where the collaborators sample from identical ports--subjected to the same gas flow (spiked plus ambient). A continuous monitor is attached to the spiked and unspiked sampling manifolds to monitor the integrity of the spike. The collaborators sample ambient air simultaneously at an identical sampling manifold that is at a similar location in the unspiked section. The gas in both sections is then exhausted to the outdoors.

DESIGN FACTORS

The design of the NO_2 , ambient-air sampling system was based on the following factors:

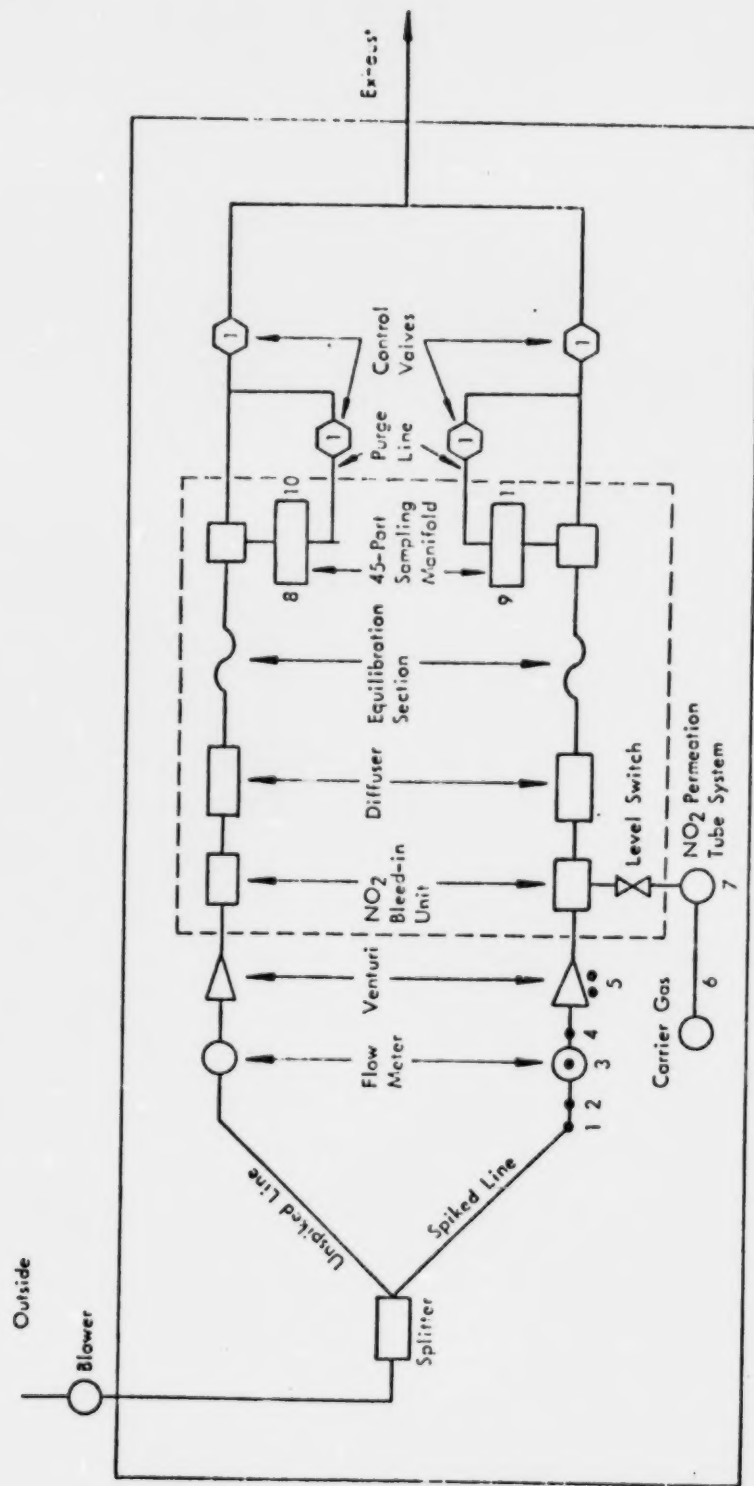
1. The flow rate of each of the four methods to be tested is approximately 0.2 liter/min, with a maximum of 1 liter/min for some of the instruments that would be used in the instrumental methods.
2. The sampling period of each manual method is 24 hr; each instrumental method is preferably 24 hr, but could be less.
3. NO_2 permeation tubes whose rates are approximately 1 $\mu\text{g}/\text{min}$, which are furnished by the government, are the source for the spiked levels of NO_2 . These tubes are to be operated at $25.1 \pm 0.2^\circ\text{C}$.
4. The number of collaborators for each collaborative test is to be 10.
5. The NO_2 range of concern is 50 to 350 $\mu\text{g}/\text{m}^3$, which is representative of ambient conditions.
6. There are four different NO_2 spiked levels: high, low, and two medium. Each level is maintained throughout the run's period, within the accuracy of the system.
7. The test period is to be no more than 6 days, which is based upon the consensus of potential collaborators surveyed.
8. The overall NO_2 sampling system accuracy is to be 5% or better.
9. The flow control in the spiked section is to be 2% or better.

10. Flow parameters of the spiked section are to be measured.
11. One NO_2/NO chemiluminescent device, switched between spiked and unspiked sampling manifolds (or stations), is to be used as a monitoring instrument.
12. Only one person from each collaborator's organization will be needed in the field for each method.
13. There is turbulent flow in the spiked section between the point of injection of the spiked levels of NO_2 and the diffuser to provide mixing of the spiked NO_2 with the ambient air. The diffuser ensures proper mixing. Up to 20% of the stream in each section--spiked and ambient air--can be sampled to (a) ensure that there is capacity in the main stream to provide each collaborator with his needs in case there is a problem with one or more collaborators drawing an excess amount; and (b) allow the quantity of spiked flow to be drawn from the center of the spiked line where there is assurance of equilibrium. There is to be a minimum amount of adsorption of the spiked NO_2 on surfaces, from its source to and including the sampling manifold. By using Teflon or glass as the material in which the gases come in contact and by maintaining a high gas flow rate, which allows for extremely short residence times, adsorptivity of NO_2 on surfaces and reaction with water vapor and other losses are insignificant.
14. Each section--spiked and unspiked--is to be similar, including material and geometric aspects.
15. Each section is to be under positive pressure so that no unwanted air will be pulled into the system in case there were a leak.
16. Collaborator's equipment size, configuration and power requirements must be met.
17. Environmental effects on operation of sampling system must be considered.

SYSTEM DESIGN

The final design of the NO_2 , ambient-air system is shown in a general schematic form in Figure 2. Annotated photographs of this operational system are given in Figure 3.

The input to the system is located outdoors about 2 m above ground level and approximately 10 m from the building. A 1/4-in. orifice in the 2-in. aluminum tubing provides resistance to the flow of ambient air to keep the Model 8700 DMP "Tornado" blower at a stable rpm, and to serve as



Monitoring Points:

1. Flow Temperature
2. Flow Pressure at Input to Flow Meter
3. Ambient Air Flow
4. Flow Temperature
5. Pressure Drop of Venturi & Temperature of Pressure Transducer

Notes:

6. Carrier Gas Flow
 7. NO₂ Flow Temperature
 8. Port Pressure
 9. Port Pressure
 10. NO₂ & NO
 11. NO₂ & NO
1. Component within Dashed Area Made of Teflon
 2. Piping Outside Dashed Area made of Aluminum
 3. Venturis made of Stainless Steel
 4. Spiked & Unspiked Lines Symmetric with Respect to Geometry & Material

Figure 2. Final design of the NO₂, ambient-air sampling system.

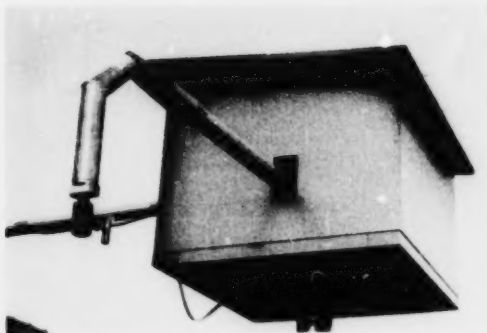


Photo 1 - Air Intake and Blower Housing. 2" Aluminum tubing. Valve on intake provides resistance to flow to keep blower at a stable rpm. Intake is 2 meters above ground level and about 8 meters from station roadway.

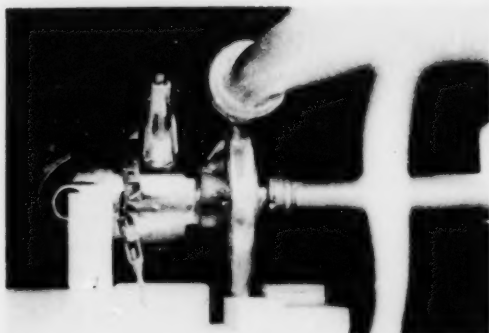


Photo 2 - Blower. Model B700 DMP. "Tamura" Series Electric Company, Chicago, Illinois.



Photo 3 - Blower Housing and 2" Line Going into Building.



Photo 4 - View from Inside Building of Line from Blower.

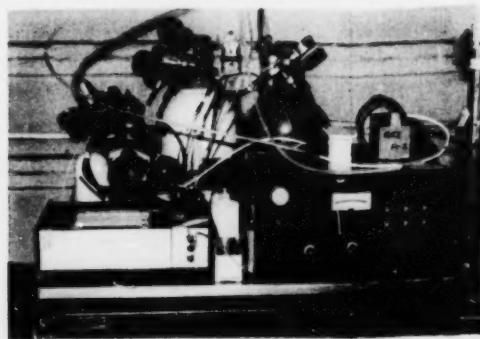
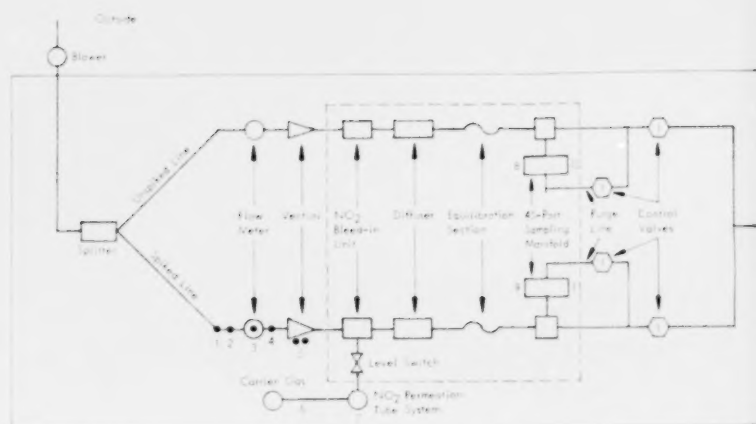


Photo 12 - Bendix Model 8D18 NCHNO₂/NO_x Analyzer Used to Monitor Levels of NO₂ and NO_x in Spiked and Pumped Lines.



Monitoring Points:

1. Flow Temperature
2. Flow Pressure at Input to Flow Meter
3. Ambient Air Flow
4. Flow Temperature
5. Pressure Drop of Venturi & Temperature of Pressure Transducer
6. Carrier Gas Flow
7. NO₂ Flow Temperature
8. Port Pressure
9. Port Pressure
10. NO₂ & NO_x
11. NO₂ & NO_x

Notes:

1. Components within Dashed Area Made of Teflon.
2. Flowing Gas Tube Dashed Area Made of Aluminum.
3. Venturi made of Stainless Steel.
4. Spiked & Unspiked Lines Symmetrical with Respect to Geometry & Material.

(A) - General Schematic of the Ambient Air NO₂ Sampling System.



Photo 5 - 2" Aluminum Tubing Going into Splitter (a) Located on Top of Metal Cabinet--Top Right of Photo.

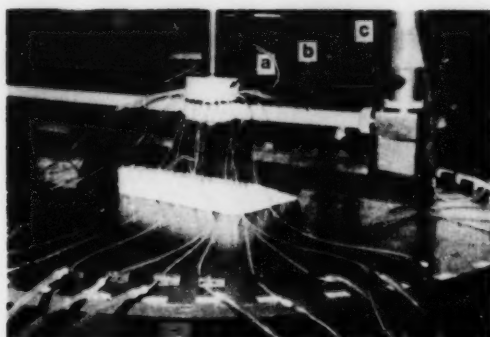


Photo 11 - Sampling Manifold (a) with Bypass Line (b) and Butterfly Control Valve (c) to Exhaust

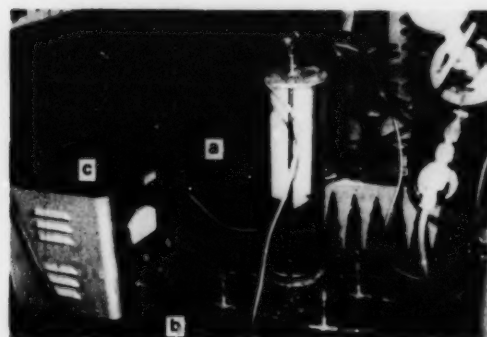


Photo 12 - Filter (a) and Control Valve Manifold (b) on Inlet Side of Permeation Tube System. Filter body is 10-cm diam. polystyrene tube 40-cm long, with brass end caps. Stainless steel needle valves on each line going to rotameters. Capacitance relay unit (c) is connected to wire around one of the thermometer stems and turns off temperature control unit (e of Photo 8B) if bath temperature exceeds 27°C.

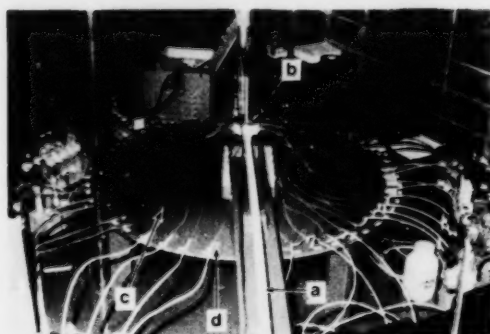
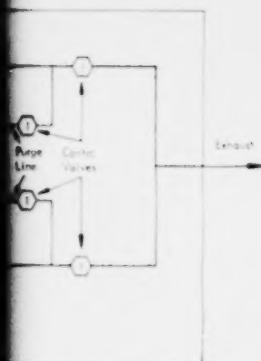
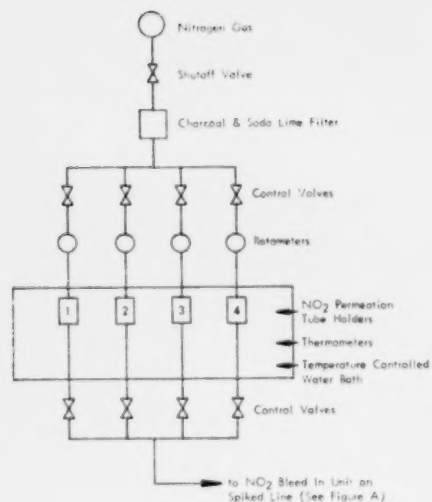


Photo 13 - 1/2 Teflon Pipe Equilibration Section (a) and Spiked Line Sampling Manifold (b). 1/8 Teflon tubing (c) connects manifold to the sampling ports (d) on circumference of upper table.



Only within Dashed Area
of Teflon
Not Side Dashed Area made
aluminum
made of Stainless Steel
Unspiked Lines Symmetric with
to Geometry & Material



(B) - Block Diagram of NO₂ Permeation Tube Assembly. Various combinations of the permeation tube holders are connected to the outlet manifold to provide the different spike levels.

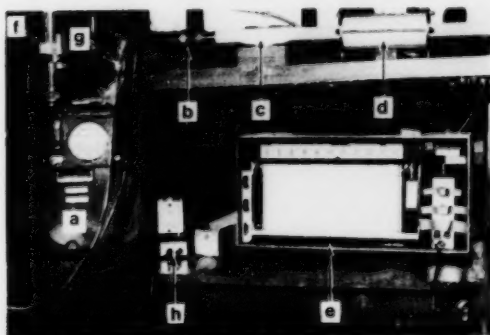


Photo 14 - Front View of Dry Gas Meter (a), Venturi (b), NO₂ Bleed-In Unit (c), and Diffuser (d). Recorder (e) is connected to thermocouples (f and g) at inlet and outlet of gas meter with switching unit (h) that alternates readings of the two thermocouples.

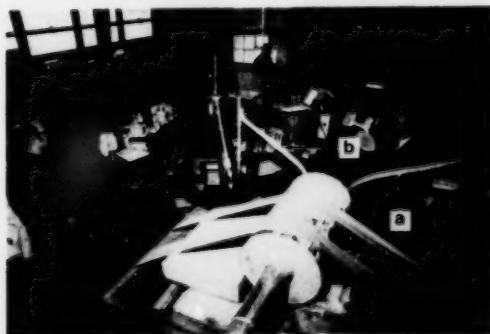


Photo 15 - Splitter with 1/2 Aluminum Tubing on Outlets to Spiked Line (a) and Unspiked Line (b). Internal baffles in splitter divide incoming airflow into two equal paths.

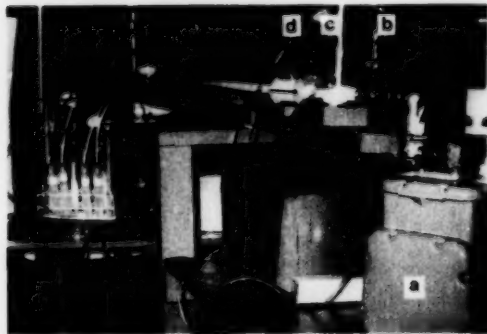
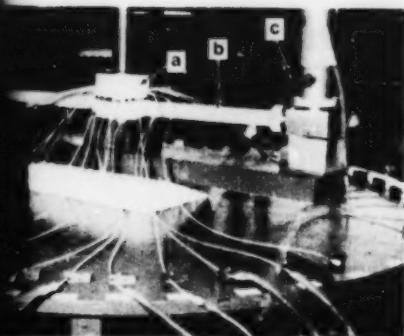
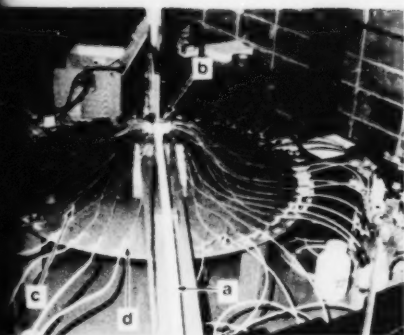


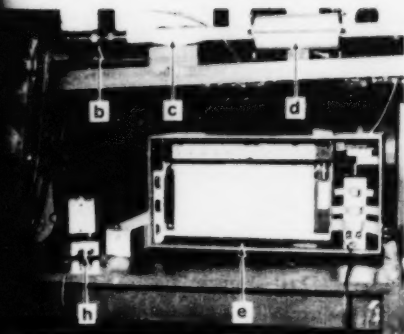
Photo 16 - Dry Gas Meter (a), Singer AL-175, American Meter Company. Stainless Steel Venturi (b), NO₂ Teflon Bleed-In Point (c), and Teflon Diffuser (d) on Spiked Line.



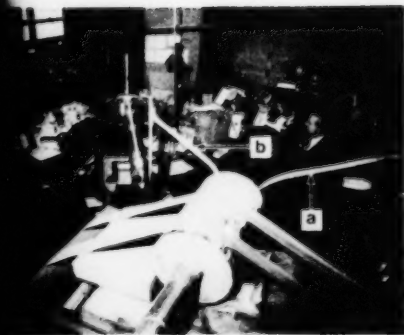
11 - Sampling Manifold (a) with Tygon line (b) and Borelli Control Valve (c) to Teflon.



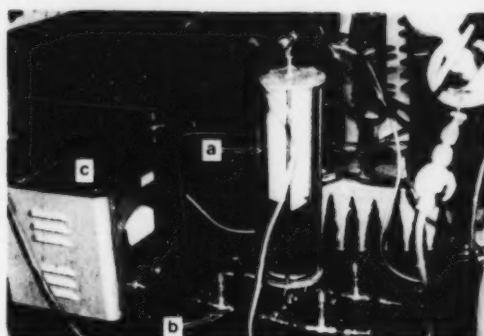
12 - Teflon flow transducer manifold (a) and spiked line sampling manifold (b). Teflon (c) connects manifold to sampling ports (d) on circumference of upper table.



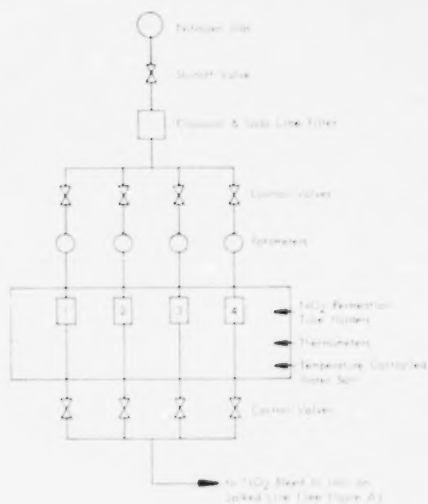
13 - Front view of Dry Gas Meter (a), Venturi (b), N_2O_2 Bleed-In (c), and Diffuser (d). Recorder (e) is connected to thermocouples (f) at inlet and outlet of gas meter with patching unit (h). High gas readings of the two thermocouples.



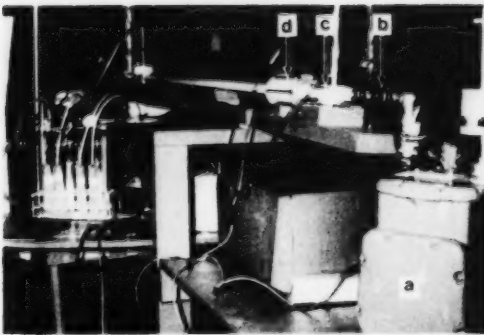
14 - Splitter with 3/16 Aluminum tubing on outlets to spiked line (a). Tygon line (b) - Teflon tubing (c) splits fluid incoming to two output ports.



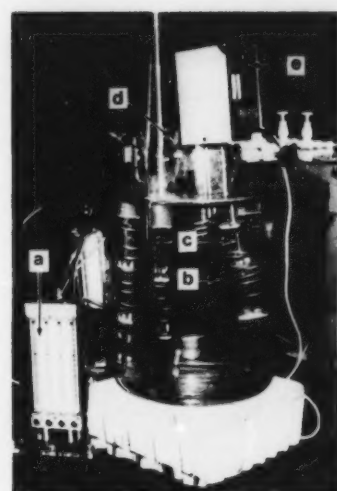
15 - Filter (a) and Control Valve Manifold (b) on back side of Permeation Tube System. Filter holds a 10cm diam polystyrene tube 40cm long with ends and caps. Ingress steel needle valves at each end going to analyzers. Capillary tubing unit (c) is connected to side around one of the thermometer stems and turns off temperature control unit (e of Photo 7B) if both temperature exceeds 27°C.



16 - Block Diagram of N_2O_2 Permeation Tube Assembly. Various combinations of the permeation tube holders are connected to the output manifold to provide the different spike levels.



17 - Dry Gas Meter (a), Singer AL-175 (b), N_2O_2 Bleed-In Point (c), and Teflon Diffuser (d) on spiked line.



18 - Permeation Tube Bath Assembly. Tygon tubing from analyzers (a) connects to copper heat exchanger coils (b) wrapped around glass jacket (c) of each permeation tube holder. Nitrogen flow comes in at bottom, flows past the permeation tubes held by Teflon spacer disks, and outside neck at top of holders (d). ASTM 0-30°F thermometers sealed into top of holders with thermometer bulbs about 4 cm below water level in bath. Temperature control/stirrer unit (e) is Model ES2N, House Instruments, Inc., Saddlebrook, N.J.



19 - Top View of Temperature-Controlled Water Bath and Permeation Tube Assembly with Teflon Manifold and Control Valves (Top Right) and N_2O_2 Feed Line to Point c of Photo 17.

a gross flow control. A Variac inside the building serves as an operational flow control. The blower is located at the input end of the system to provide positive pressure in the system. It is located outdoors to keep out the intensive noise it generates and is housed as shown in Photographs 1 and 3 of Figure 3 to protect it from the elements.

The line from the blower to the splitter is 2-in. diameter aluminum pipe. It is sufficiently long to serve as a trap for any excess moisture and to bring the ambient air to room temperature. The splitter is also made of aluminum. This splitter, shown in Figure 4, reduces large-scale turbulence from the blower and divides the ambient airstream between the spiked and unspiked 1-in. diameter aluminum lines. A controlled flow goes to the venturi where the air flow in the spiked line is continuously measured and recorded. This flow is determined by the following equation:

$$\begin{aligned} \text{Flow in liters/min} &= \frac{\text{method sampling rate (number of samples} \times \text{number} \\ &\quad \text{of collaborators} + \text{monitor number} + \text{purge number})}{\text{percent flow drawn through sampling manifold}} \\ &= \frac{0.2 \text{ liters/min} \times (4 \text{ samples} \times 10 \text{ collaborators} + \\ &\quad \text{1 NO/NO}_2 \text{ monitor} + \text{purge-line flow})}{\text{percent flow drawn through sampling manifold}} \\ &= \frac{0.2 (4 \times 10 + 1 + 4)}{0.15} = \frac{9}{0.15} = 60 \end{aligned}$$

The monitor number and the purge number are flows attributable to the continuous monitor and the purge line of the system, respectively. The flow on each line--the spiked and unspiked--is turbulent--Reynolds No. > 2,100 --with the Reynolds number being

$$\begin{aligned} R &= \frac{Q}{LVD} = \frac{Q \text{ liter/min} \times 1,000 \text{ cm}^3/\text{liter}}{0.785 \times 0.15 \text{ cm}^2/\text{sec} \times D \text{ sec} \times 60 \text{ sec/min}} \\ &= \frac{1,000 Q}{7.065 D} = \frac{1,000 \times 60}{7.065 \times 2.1} = 4,000. \end{aligned}$$

Since the spiked and unspiked sections are identical except that the spiked section also contains the monitoring points 1, 2, 3, 4, and 5 identified in Figure 2 and the NO₂ permeation-tube system, only the spiked section will be discussed.

From the splitter, the spiked line connects to a Singer AL-175 dry-gas meter, which is made by the American Meter Company. (See Photograph 9 of Figure 3.) This flow meter has a pressure drop of 10 mm of water and is temperature compensated. Thus, only the gas pressure is measured to correct the flow readings to obtain the true flow rate of ambient air

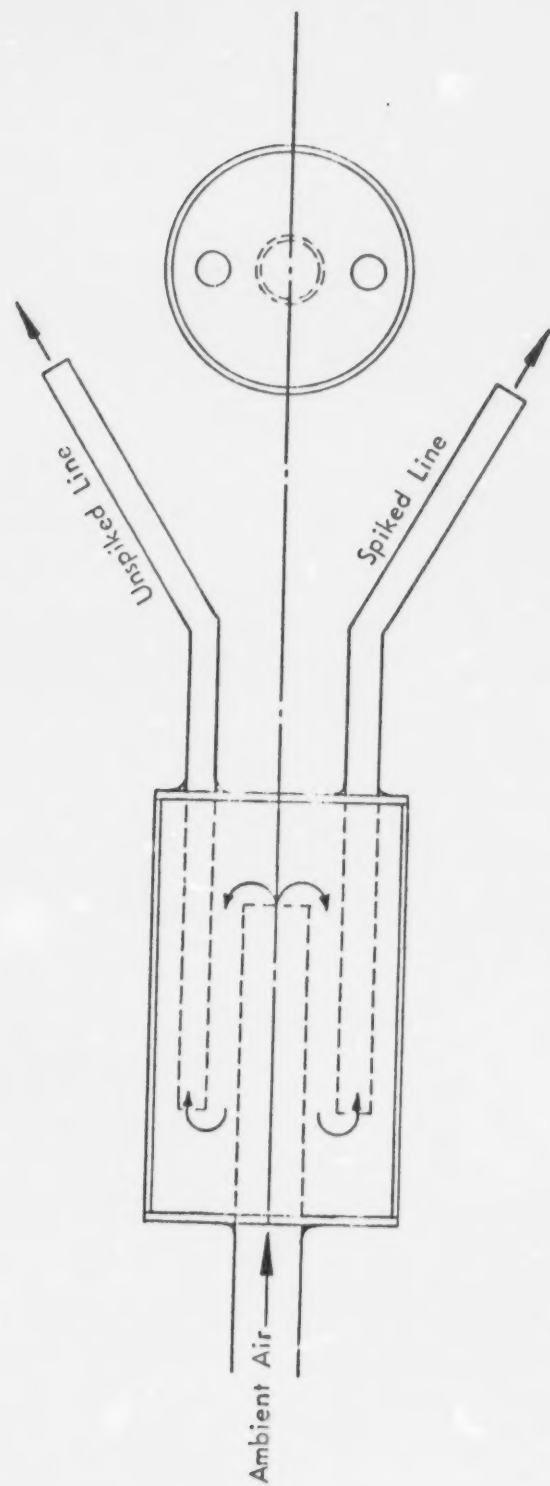


Figure 4. Ambient-air stream splitter.

delivered during a test run. This flow rate is determined hourly by measuring the time required for a known quantity of air to pass through the meter.

The output of the flow meter is connected, as shown in Photographs 7 and 9 of Figure 3, to a stainless-steel venturi, which was designed for a flow of 60 liters/min. This venturi is used as a general flow-control device, and provides a continuous record of flow rate using a strain-gage pressure transducer and thermocouples--see Point 5 of Figure 3(A). Both the pressure drop of the venturi and the temperature of the pressure transducer are recorded on analog recorders. Control of the flow rate is handled by monitoring the venturi pressure drop. When the value deviates from a reference value, 60 liters/min, the flow rate can be changed appropriately by making an appropriate adjustment of the Variac control to the blower.

The flow temperature measurement (Point 4 of Figure 3(A)) is actually the gas-flow temperature at the output of the gas meter and at the input to the venturi, since those two units are physically close together (about 12.5 cm apart). Tests have shown that the temperature at this point is identical with the temperature at the gas flow meter inlet. The gas temperature at this point is normally within 0.5°C of room temperature. This temperature measurement is used to obtain accurate gas-flow values.

To provide more accuracy, the thermocouples at Points 2 and 4 of Figure 3(A) were replaced for this test by a 0 to 50°C bimetallic dial thermometer that is located at Point 4 of Figure 3(A).

The output of the venturi is a few centimeters from the input of the NO₂ bleed-in unit as shown in Photograph 9 of Figure 3. These two units are connected by 1.0-in. diameter aluminum tubing. From the input of the NO₂ bleed-in unit through the sampling manifold, the system is made of Teflon.

The NO₂ bleed-in unit, as shown in Figure 3(A) and Photographs 7 and 9 of Figure 3, receives ambient air from the venturi and a level of NO₂ (a spike) from the NO₂-permeation tube assembly (see Figures (A) and (B), and Photographs 8 a-c of Figure 3). Detailed photographs of this bleed-in unit are given in Figure 5. Photograph 1 of Figure 5 is a closeup showing the assembled Teflon unit with its metal holding/mounting plates. The gas stream, or ambient air, enters the opening to the right and passes through the unit, mixing with the spiked level of NO₂ which exits through the tapered smaller tubing shown as concentric to the output of the bleed-in unit at the left of Photograph 1 of Figure 5. The vertical tube of this bleed-in unit accepts the NO₂ gas from the permeation-tube assembly. This spiked gas flows downward through this tube, which is inside the unit (see

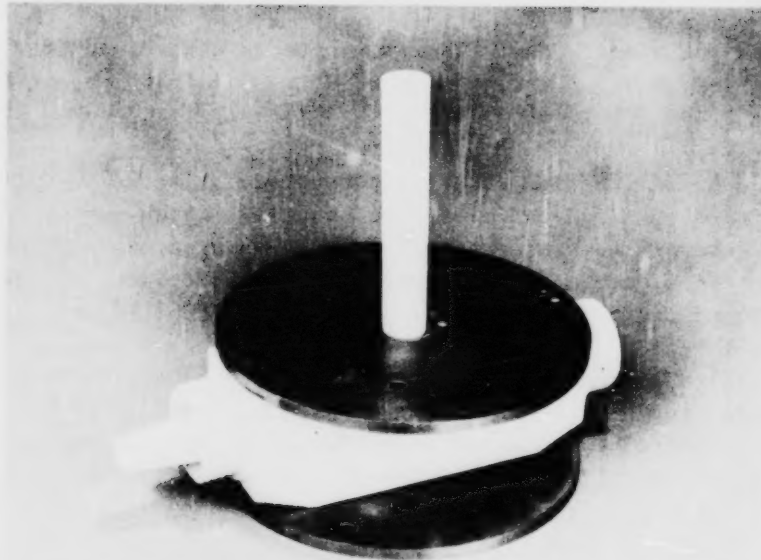


Photo 1 - Detail of NO₂ Bleed-In Unit with Vertical Tube from Permeation Assembly, Chamber with Central Tapered Pickup Tube and Stainless Steel Mounting Components.

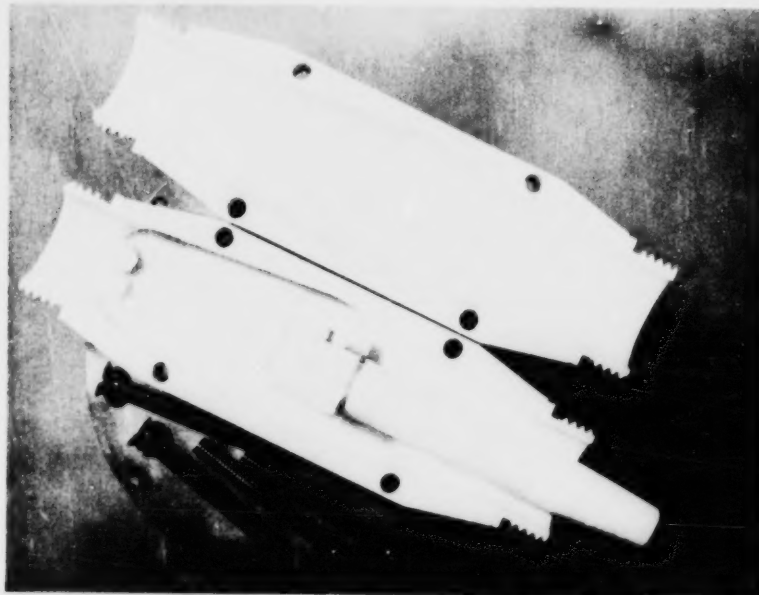


Photo 2 - Close-Up Showing Machined Chamber with Pickup for Bleed-In in Place.

Figure 5. Photographs of the NO₂ bleed-in unit-- assembled and disassembled.

Photograph 2 of Figure 5), and after a short run, mixes with the ambient air as stated before.

The NO₂-permeation system is shown in Figure 6 and Photographs 8 a-c of Figure 3. Details of the system are given in the captions of these photographs. The nitrogen carrier gas is used to flush the NO₂ into the system. It is passed through a charcoal and soda-lime scrubber before it is delivered to the NO₂ permeation tubes. Also, the flow is set by means of control valves and rotameters. This flow is monitored during system operation. The carrier gas is then fed into four separate branches to achieve different levels of NO₂. (More detail on the permeation tubes and their arrangements in the branches is given in Appendix B.) The NO₂ permeation tubes^{1/} are arranged in these four different branches to provide NO₂ spike levels of approximately 50, 100, 200 and 300 µg/m³. Branch 1 has four permeation tubes, Branch 2 has five permeation tubes, Branch 3 has two permeation tubes, and Branch 4 has two permeation tubes. An ASTM calibrated thermometer (0.1°C or better accuracy) is an integral part of each permeation-tube branch. Each set of permeation tubes is enclosed in a glass tube which has an inlet for the nitrogen carrier gas and an outlet for the nitrogen carrier gas/NO₂ mixture. These NO₂ permeation-tube enclosure units are immersed in a temperature-controlled water bath for operation at 25.1°C. If the temperature of this bath were to vary more than 0.2°C, a correction would be made from the following relationship:

$$\text{Log } r = 0.034857 (273.12 + T) - 10.29198,$$

where T = temperature in °C of the permeation-tube environment, and

r = the permeation rate.

Flow meters of the permeation-tube assembly that measure the nitrogen flow were calibrated by the manufacturer to 1% accuracy. Thermometers that were used to measure the gas temperature in the permeation-tube holders are ASTM type that are accurate to within 0.1°C. The permeation tubes used were calibrated by the National Bureau of Standards and checked by EPA. (See Appendix B.) The entire permeation assembly from the tube holders to the pickup fitting, where the spiked gas enters the main gas stream, was checked for leaks with Snoop and found to be airtight.

^{1/} "Operation Characteristics of NO₂ Permeation Device," by Harry L. Rook, Ernie E. Hughes of NBS, Washington, D.C., and Robert S. Fuerst and John Margeson of EPA, Research Triangle Park, North Carolina. A paper presented before the Division of Environmental Chemistry, American Chemical Society, Los Angeles, California, March 31 to April 5, 1974.

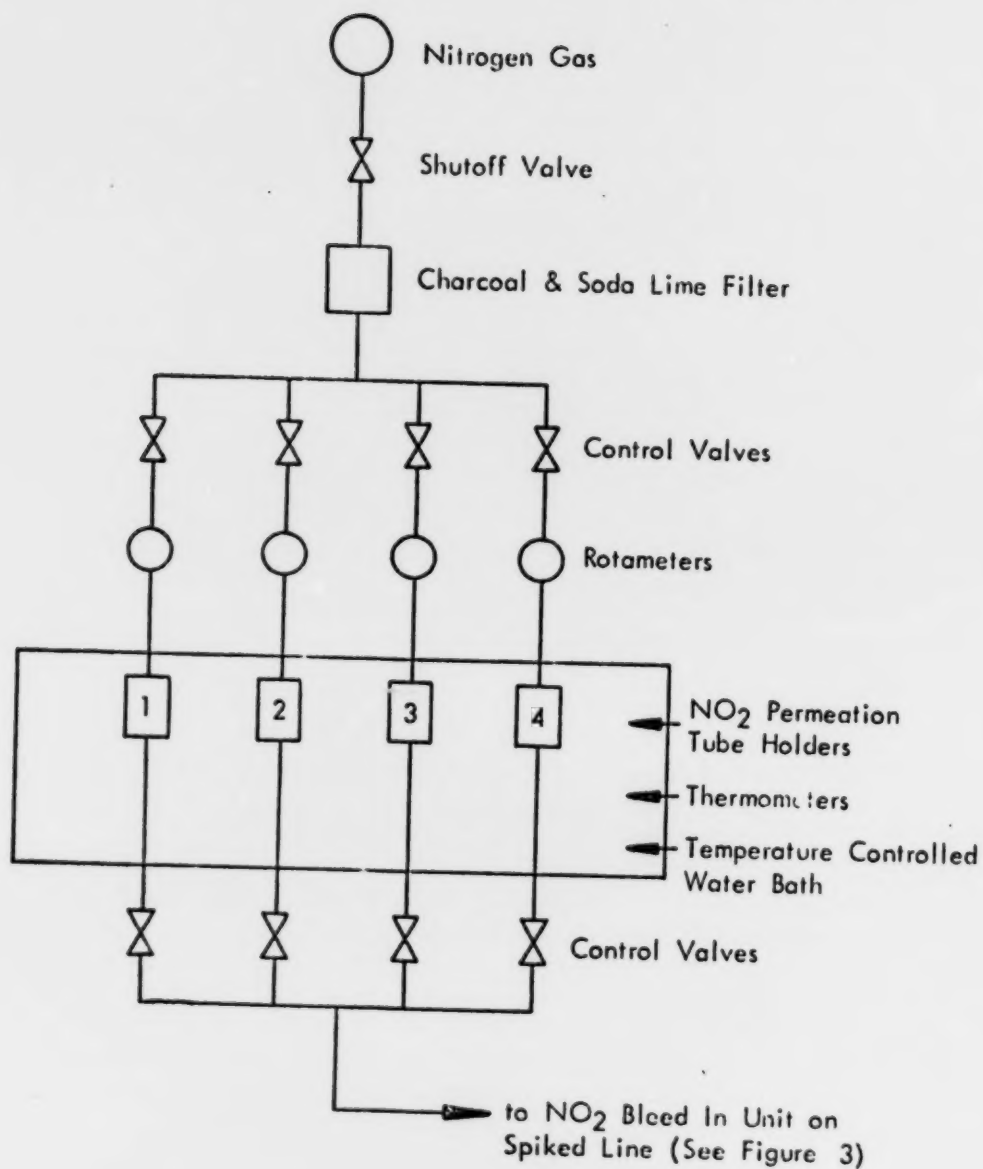


Figure 6. Schematic drawing of the NO₂ permeation tube assembly.

The ambient air and the NO_2 spike flow from the bleed-in unit to the diffuser where they are well mixed. The diffuser is a few centimeters downstream from the bleed-in unit, as shown in Photograph 9 of Figure 3. At the diffuser, shown schematically and in the photograph in Figure 7, the gases enter the diffuser through the Teflon tubing (Section A of the schematic drawing of Figure 6), pass into the spiraled tube and through its angled holes into the space outside the tube. The flow continues through the holes in the prescreen block, Item D of the schematic, and then through a series of Teflon screens, Item E.

The homogeneous mixture passes through an equilibration section that is Teflon tubing 1.0 m long. This section of tubing provides the final equilibrated concentration. This tubing is connected to the input of the sampling manifold. (See Photographs 10 and 11 of Figure 3.)

The 45-port sampling manifold is constructed of Teflon except for its metal plates which are entirely external. Photographs 1 through 3 of Figure 8, which show external and internal views of the sampling manifold and a schematic drawing, describe the operation of the manifold. The stream of the homogeneous mixture of ambient air and a spiked level of NO_2 flows through the bottom portion of the manifold into the exhaust line. Section A of the manifold is in the pickup tube through which flows the total volume of gas sampled by the collaborators. The inlet of this pickup tube is located such that this volume is drawn from the central portion of the main stream. The sampled volume flows past a mixing impeller (B) and then into the main chamber (C) of the manifold. In this chamber, the flow is spread evenly to the 45 symmetrically located exit channels (D). The gas in the main chamber that is not drawn through the exit channels to the collaborator port flows out the exhaust duct or purge line which has a control valve. Both exhaust lines from the manifold join downstream to form a common exhaust tube, which also contains a flow-control valve.

One port of each sampling manifold is used to monitor the pressure in the sampling manifold to determine if it remains positive (see schematic drawing of Figure 3). Another port of each manifold is used to monitor the NO_2 and NO levels being sampled by the collaborators. A Bendix Model 8101 B chemiluminescence $\text{NO-NO}_2\text{-NO}_x$ analyzer is used for this and is switched between the spiked and unspiked manifolds. (See Photograph 12 of Figure 3.)

SYSTEM CHECKOUT

Readyng the system for the collaborative test comprised three principal areas of activity: (a) determination of levels of NO and NO_2 , both ambient and inside the building; (b) checkout of the sampling system, including monitoring devices and test instrumentation; and (c) checkout of



Photo 1 - Top View Diffuser Components: Housing, End Sections, Spiraller Tube, Teflon Screens, Retaining Rings.

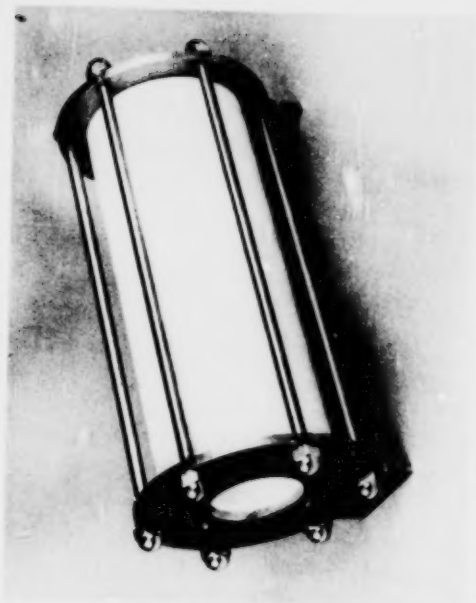
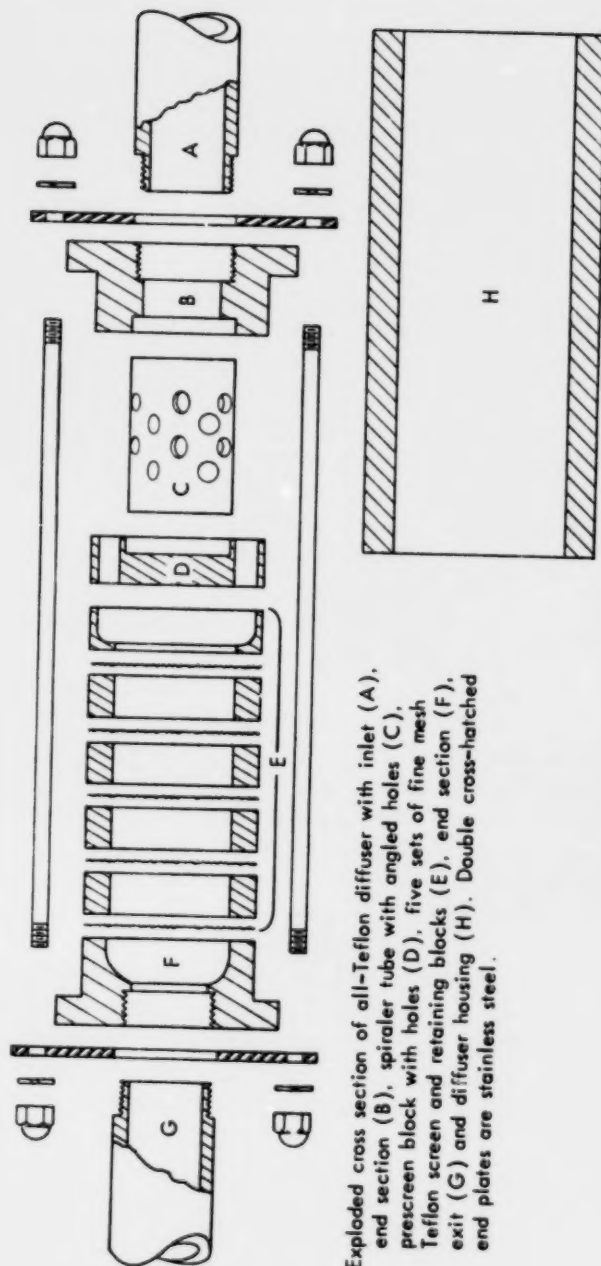


Photo 2 - External View of Diffuser.



Exploded cross section of all-Teflon diffuser with inlet (A), end section (B), spiraller tube with angled holes (C), prescreen block with holes (D), five sets of fine mesh Teflon screen and retaining blocks (E), end section (F), exit (G) and diffuser housing (H). Double cross-hatched end plates are stainless steel.

Figure 7. Schematic drawing and photographs of the diffuser.

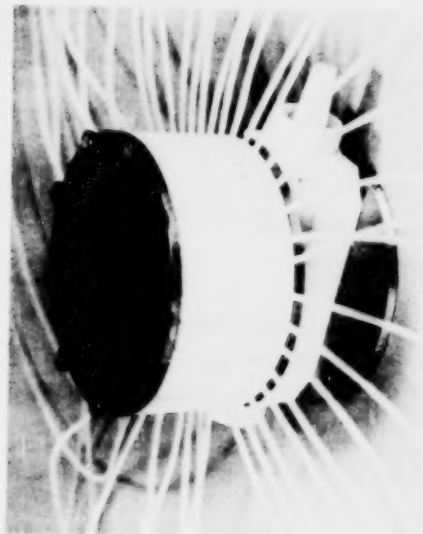


Photo 1 - Sampling Manifold External View.

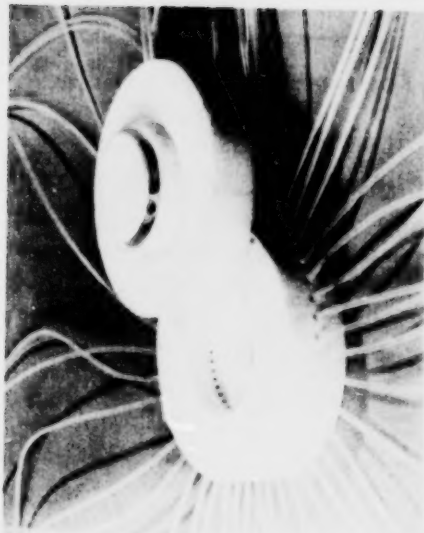


Photo 2 - Internal View (Right Component is Inverted in this Photo).

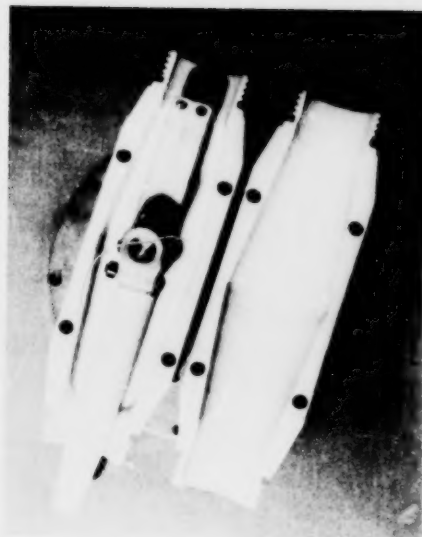
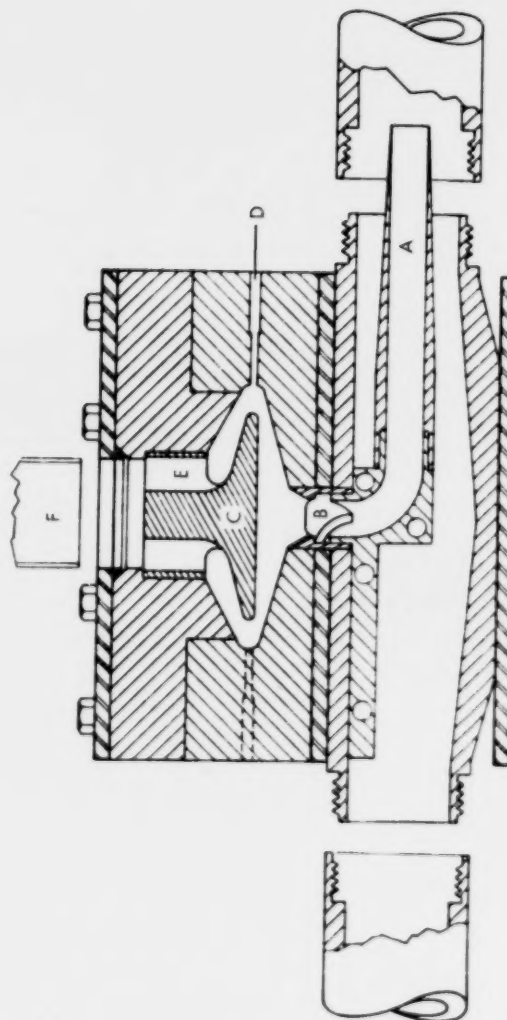


Photo 3 - Internal View of Manifold Pickup Section Showing Flow-Spiraling Impeller.



Cross section of all-TFE Teflon manifold with pickup tube (A), mixing impeller (B), main chamber flow spreader (C), exits to collaborator ports (D), channel to exhaust manifold (E), and manifold exhaust duct (F). Gas not captured by pickup assembly exhausts at left side of manifold base. Double cross-hatched assembly plates at top, middle, and bottom are stainless steel.

Figure 8. Schematic drawing and photographs of the sampling manifold.

the sampling system as an operational system. These three areas are discussed below.

Ambient Levels of NO and NO₂

Ambient levels of nitrogen oxides at the test site were generally low, but there were considerable variations at these levels. Since the test site is located in a rural area south of Kansas City where there is very little industry, the primary factors that influence NO_x levels at the site are wind speed and wind direction.

During tests of NO_x levels using MRI's Bendix Model 8101 B chemiluminescence NO-NO₂-NO_x analyzer for 24-hr monitoring, the lowest levels were found when the wind was from the south. Both NO and NO₂ seldom exceeded 20 µg/m³. Periods of more than 1-hr duration were measured when readings were indistinguishable from the purified zero gas used to calibrate the analyzer.

With northerly winds, NO₂ levels were generally between 30 and 50 µg/m³ and NO levels were approximately 10 µg/m³. As expected, the ambient levels followed an inverse relation with respect to wind speed. The highest daily readings were coincident with the morning and evening rush hours. These peak levels generally began at about 7:00 a.m. and again at 5:00 p.m. and lasted between 2 to 4 hr.

The highest recorded levels of NO occurred under calm wind conditions when the light vehicular traffic in the vicinity of the test station generated levels in excess of 100 µg/m³. NO levels did not exceed NO₂ levels at this site.

Over a 24-hr period, average NO₂ levels were 10 to 50 µg/m³, and NO levels were of the order 10 to 20 µg/m³. During any 24-hr period, maximum NO₂ levels were generally several times higher than the minimum levels. Thus, while NO₂ levels at the test site are lower than those at urban, industrial locations, the NO₂ levels do exhibit the variability found under normal ambient conditions. Indoor readings were similar but did not show the sudden changes often found when monitoring outdoor levels.

Subsystems and Units

The venturi and dry-gas meter were calibrated using a 1.0 ft³/min wet-test meter. Information concerning the calibration is given in Appendix C. The entire system was prepared for the test by bringing all components to normal operating conditions several days prior to the test and running the system continuously in this mode until the beginning of the test. Water addition to the constant-temperature bath was the only

maintenance required. The temperature variation of the permeation-tube bath during this time was less than 0.1°C. A check of NO_x levels in the cylinders of prepurified nitrogen carrier gas found no NO₂ and 40 µg/m³ NO.

The Bendix NO_x analyzer was checked at MRI by a Bendix field representative. The difference in spiked and unspiked readings of the Bendix analyzer agreed within 10% of the calculated spike levels at all four levels used for the test. The instrument was stable and reliable when operated continuously at the levels found during normal testing. Checks with calibration gases reveal that the catalytic converter efficiency does fall off sharply above 400 µg/m³.

The symmetry of the sampling ports was checked in two ways. The primary way was that the pressure drop at each port was measured under the normal load of 200 cc/min. This test showed that all ports gave a pressure drop of 1.5 cm of water ± 0.5 cm. Such a pressure drop should have no effect on normal sample flows and the flow rates from the ports should be identical to that obtained by pulling free room air into the sampling trains. However, since analyzers for this test required flow rates greater than 200 cc/min, larger Teflon tube connections were provided on each manifold. These lines were capable of supplying more than 2 liters/min without developing a pressure drop of 1.5 cm of water.

A second way was to connect the NO₂ monitor to ports of the spiked and unspiked sampling manifolds and measure the level of NO₂ in micrograms per cubic meter. This was done in two ways: the system under a load, e.g., a spiked level of approximately 350 µg/m³; and an unloaded condition where just ambient air was passed through each section--spiked and unspiked--of the NO₂ sampling system. In both cases, the NO₂ monitor showed no variation between four ports spaced equally around the manifold.

System Operation

Identical materials and dimensions are used on the spiked and unspiked sections of the NO₂ sampling system. Handling and treatment of all components were also identical.

Flow rates of the spiked and unspiked sides were within 10% of each other with all dampers open. In normal operation, the exhaust dampers are adjusted to give a positive pressure of 2 to 4 mm water at the sample manifolds. Once set, this pressure is stable.

The rise and fall times to equilibrium in response to changes in a spike level were checked. Rise time was less than 15 min and fall time was less than 5 min (when permeation tubes were disconnected). The fall

time is essentially that of the analyzer response time, allowing for the purge time of the sample lines. The rise time is longer than the fall time because of the increased pressure against which the carrier gas stream must work when a set of permeation tubes are connected. Some flow reversal in the permeation-tube holders occurs after connection.

Since the response times were essentially limited by flow rates and instrument response, no observable adsorption effects were noted. Checks of NO_x levels found at the sampling ports agreed, within normal accuracy limits, with those measured outside the building. At the $50 \mu\text{g}/\text{m}^3$ level both readings were within $5 \mu\text{g}/\text{m}^3$ (0.5% of full scale), which is within the accuracy of the monitoring instrument. Thus, the unspiked samples at the sample ports accurately reflect ambient levels and the sampling system may be considered to be inert with respect to NO_2 .

TEST SITE

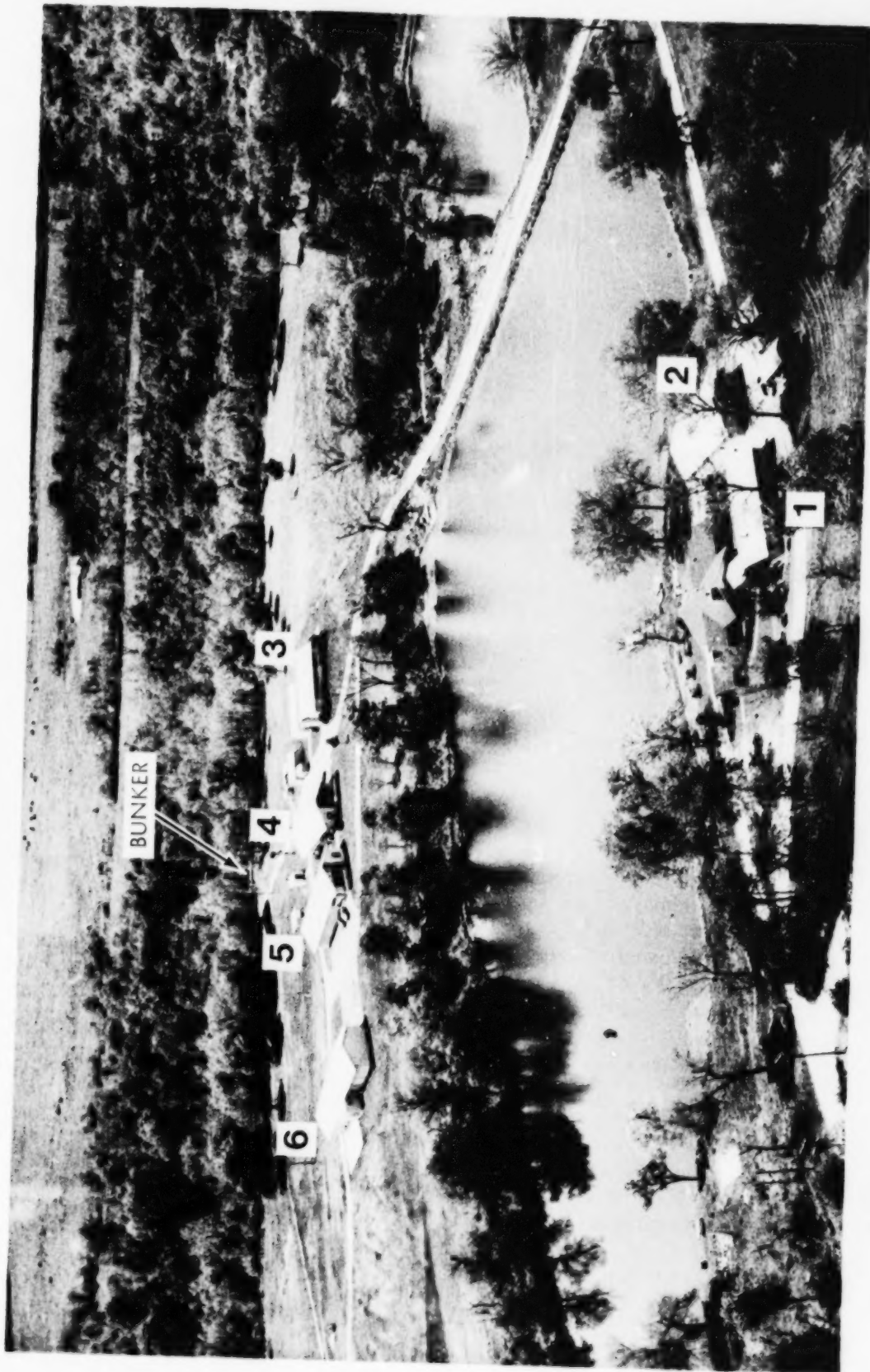
The general criteria one would use in selecting a site include the ambient level of NO_2 and variations thereof, general meteorological and climatological conditions, work facilities for the collaborators (adequate space, facilities, housing, etc.), cooperation of the organization furnishing the site, logistic aspects, and local lodging accommodations.

The levels of NO_2 required are those representative of ambient NO_2 conditions, which are in the range of a few micrograms per cubic meter to $350 \mu\text{g}/\text{m}^3$. These levels could be achieved at one site with a low level of NO_2 by spiking the ambient air with various levels of NO_2 in a manifold sampling system.

MRI's field station (see Figure 9) which is located in a rural area south of Kansas City, meets all the criteria and was selected as the test site. The NO_2 ambient-air sampling station is housed in Building 3, shown in Figure 9. The input to the sampling system is located outside the building near the roadway (see Photograph 3 of Figure 3).

The test facilities are described in conjunction with the sampling system. Photographs of the facilities are given in Figure 10. Photograph 1 shows the circular tables that house the sampling manifolds (Photograph 2) and the collaborators' sampling trains. Each table--spiked and unspiked--has a multiplicity of AC power receptacles, with each collaborator having its own branch outlets. (Each branch has its own circuit breaker and branch indicator.) This arrangement is to protect other collaborators in case one collaborator has a power failure due to faulty equipment.

Photograph 1 of Figure 10 gives a close-up view of some of the collaborators' trains positioned in their table areas (see Figure 11). Since each collaborator had only one instrument, Teflon or polypropylene tubing was run through the 2-in. pipe, which spanned the two test tables, to the other manifold (see Photograph 1 of Figure 10). This allowed the instruments to remain in one place during tests and yet sample from either the spiked or unspiked line by simply switching lines.



DERAMUS FIELD STATION

Figure 9. Collaborative test site: MRI's field station.

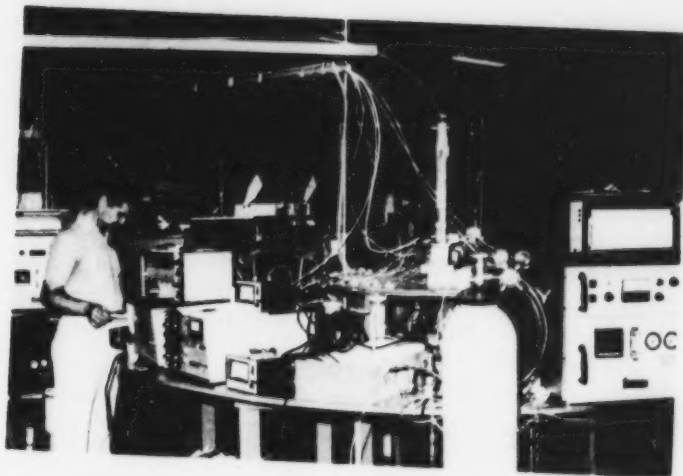


Photo 1 - Test Tables with Collaborators' Instruments

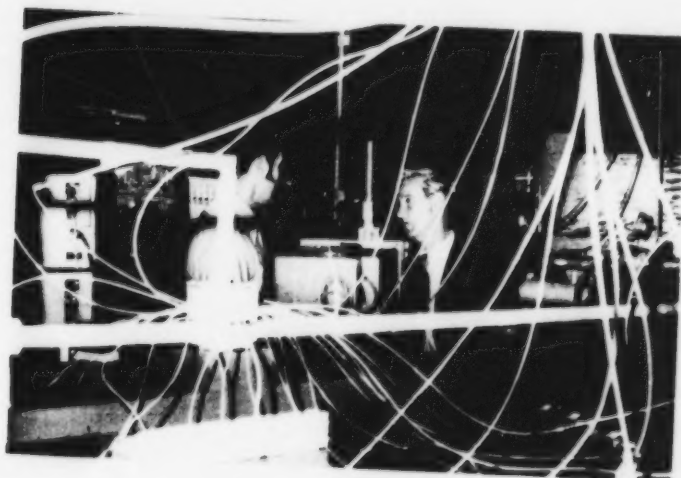
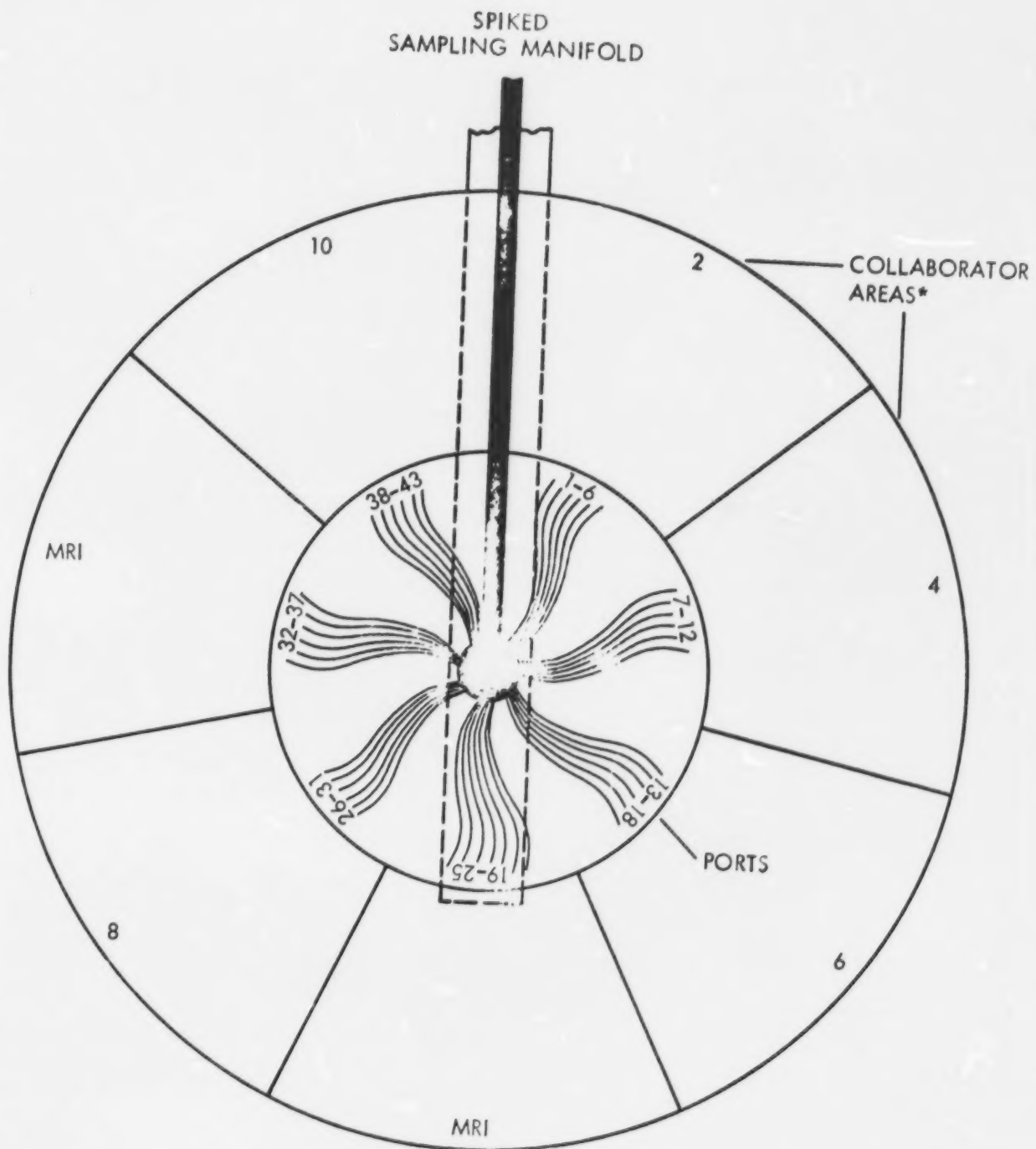


Photo 2 - Close-Up of Sampling Manifold and Collaborators' Lines Attached to It.

Figure 10. Test facilities and collaborators' instruments.



* Unspiked manifold layout similar (see Appendix F).

Figure 11. Collaborators' sampling areas at the test site.

The windows on the north side of the building were boarded to keep electromagnetic radiation from entering the building. With this blockage and a temperature control system in the building, the 25.1°C permeation bath was able to be maintained at that temperature throughout the four 24-hr runs with no detectable deviation from the 25.1°C temperature, except for a few hours when the deviation was 0.1°C.

SELECTION OF COLLABORATORS

A principal activity was to compile a list of potential collaborators and from this list select 10 to perform the testing according to the tentative Chemiluminescent Procedure. Information was obtained from EPA (names and addresses of 150 organizations) and from MRI's files to compile a list of nearly 200 potential collaborators.

A letter was sent to 162 organizations seeking their desire to participate as a volunteer collaborator on this test and evaluation program. Attached to this letter was a "Collaborator Form" to be completed which surveyed their experience with the four methods, methods they had used, equipment they could make available for the tests, acceptable length of test period, etc. A second letter was sent to those who expressed interest in the Chemiluminescent Procedure after a test date was selected. These collaborators were requested to submit certain information as well as to do some ambient sampling according to the procedure and submit their results for our evaluation. After the 10 collaborators were selected, they were apprised by letter of their selection and given pertinent information about the test. A copy of these letters and the collaborators form are given in Appendix D.

A majority of the responses indicated the desire that a test period for a method be no more than 6 days.

Nine organizations* were selected for the Chemiluminescent collaborative test from those organizations that responded in the affirmative to participate in the test. The selection was based upon the following criteria:

1. Willingness to participate on a volunteer basis.
2. Technical capabilities.

* One organization provided two collaborators, each of whom had his own equipment and worked entirely independent of each other.

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3. Related past experience.

4. Availability.

5. Ability to furnish sampling equipment, instruments, and materials required to perform the test strictly according to the method.

6. Type of organization (industrial, educational, governmental--local, state, federal--etc.).

The information needed to make the selection based on the above criteria was obtained from the collaborator forms that were returned, and from subsequent telephone conversations with the candidate collaborators.

The organizations selected as collaborators for the Chemiluminescent collaborative test were:

Air Quality Evaluation Division
Measurements and Analysis Programs
Texas Air Control Board
8520 Shoal Creek Boulevard
Austin, Texas 78758
Mr. Robert Richardson

Institute of Gas Technology
3424 South State Street
IIT Center
Chicago, Illinois 60616
Mr. Jon Zimmer

Air Pollution Control Directorate
Environmental Health Centre
Tunney's Pasture, Ottawa, Ontario, Canada
Mr. William Findlay

Montreal Urban Community
Department of Air Purification
and Food Inspection
1125 Ontario Street East
Montreal 132, Quebec, Canada
Mr. Roger Ellard

Air Pollution Control District
of Jefferson County
400 Reynolds Building
2500 South Third Street
Louisville, Kentucky 46208
Mr. Jim Harris

Air Pollution Control District
County of Los Angeles
434 South San Pedro Street
Los Angeles, California 90013
Mr. John Higuchi

Kennecott Copper Corporation
P.O. Box 11299
Salt Lake City, Utah 94111
Dr. Melvin Ken Muir

National Environmental Research Center
Environmental Protection Agency
Research Triangle Park
North Carolina 27711
Ms. Carol Ellis
Mr. Vinson L. Thompson

Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110
Mr. Bruce DaRos

These organizations will be referred to as Collaborators A through J, without specifying which is A, B, etc., to allow the organizational data to remain anonymous.

STATISTICAL DESIGN

GENERAL CONSIDERATIONS AND COMMENTS

The purpose of this collaborative test was to determine the precision and bias of the Chemiluminescent Procedure. A major element of the collaborative test was to have an experimental design that would allow this purpose to be met. Considerations that formed the bases of this design, which is given later in this section in a formal manner, are:

1. Challenge (spike) levels of NO_2 ,
2. Ambient levels of NO_2 ,
3. True values of NO_2 ,
4. Sampling time of a run,
5. Test period of the method,
6. Number of collaborators,
7. Number of samples per run,
8. Interferences,
9. Adsorptivity,
10. Sampling ports, and
11. Instrumentation.

Challenge spike level of NO_2 is an experimental design variate. Four levels of challenge were selected based upon the normal range of values found in ambient air on a 24-hr average basis: one low level on the order of $50 \text{ } \mu\text{g}/\text{m}^3$; two medium levels, one near $100 \text{ } \mu\text{g}/\text{m}^3$ and the second near $200 \text{ } \mu\text{g}/\text{m}^3$; and one high level of approximately $300 \text{ } \mu\text{g}/\text{m}^3$. A challenge

level should be steady state, or continuous at a specific level, plus or minus acceptable deviations--less than $\pm 2\%$.

Ambient levels should be lower than the lowest challenge (spike) level (approximately $50 \mu\text{g}/\text{m}^3$). Since the ambient levels are the actual ambient levels of NO_2 at the test site, those levels present during the time of testing may vary from these criteria. The ambient levels will be mixed with the challenge levels to provide the spiked challenges. There will be just ambient challenges which are identical with the ambient portion of the spiked challenges. The collaborators will sample both spiked and unspiked challenges.

For a run, the true value of NO_2 sampled by the collaborators will be taken as the NO_2 spiked level generated by the permeation-tube assembly plus the average value of the ambient challenges sampled at the same time. The error involved here adds to the overall error in the analysis.

Ten collaborators were deemed to be sufficient to obtain a cross-section of the population of the type organizations that would be involved in sampling NO_2 , be within acceptable project costs, and provide statistical significance with the results.

Adsorptivity is of concern because of the possibility of error in the NO_2 level received by the collaborators' sampling devices in contrast to the known level of the challenge--from both the standpoints of increasing and decreasing the challenge level from run to run. Teflon material was used from the NO_2 bleed-in port through the sampling manifold to minimize if not eliminate the adsorptivity factor. For further assurance, prior to commencing a run, the challenge could be run for a sufficiently long period so that all surfaces exposed would have reached a state of equilibrium with the new concentration. Both aspects were covered; Teflon was used in the construction and sufficiently long challenges were made to the system prior to commencing a run.

The port-to-port effect did not need to be incorporated in the experimental design because results of the evaluation of the NO_2 , ambient-air sampling system indicated that all ports were identical.

The major considerations with regard to instrumentation for the Chemiluminescent collaborative test were: (a) MRI would only instruct the collaborators that they are to use the sampling equipment and calibration specified in the method write-up; and (b) MRI's monitoring instrumentation and test instrumentation used in the calculation of the NO_2 , ambient-air system was sufficiently reliable and accurate. In both cases, all requirements were met.

THE DESIGN

Since some spiked readings were being taken throughout the test, but ambient readings were only sometimes obtained, there were two experimental designs used.

One statistical model applies to all the spiked readings, but does not incorporate any ambient observations. In other words, all precisions of interest were estimated, but no accuracies (biases) were determined.

This analysis of variance model is:

$$X_{ijk\ell} = \mu + C_i + t_j + L_k + e_{\ell}(ijk)$$

where μ = overall mean

C_i = i^{th} collaborator, $i = 1, \dots, 10$

t_j = j^{th} hour, $j = 1, \dots, 20$

L_k = k^{th} NO_2 level, $k = 1, \dots, 4$

$e_{\ell}(ijk)$ = measurement error in ℓ^{th} reading in ijk^{th} cell, $\ell = 1$ for every ijk .

Since the NO_2 level may change from hour to hour, there are no replicates in this framework ($\ell = 1$ always). Also, some cells are missing altogether (because sometimes a collaborator was on the ambient line and did not get a spiked reading). Each collaborator measured the spiked line only (a maximum of) 17 out of the 20 experimental hours. So all effects have to be "adjusted" for this sample imbalance.

Therefore, the general analysis of variance was performed.* (In practice, four such analyses were performed (one per level) because it turned out that the repeatability of the method depended on the NO_2 level.)

The second experimental design model describes the data set of 6 to 7 hr/run when both ambient and spiked readings were taken (by different collaborators of course).

Since the hourly variation in ambient NO_2 is significant, a "true" value was constructed for each of the 6 hr (per level). That is, for each hour, the true value was estimated as the spiked NO_2 amount plus the

* See Appendix E for a discussion of this general analysis.

average ambient reading in that hour. During these 6 hr, one-half of the collaborators measured the spiked line and the other half observed ambient. The roles ambient versus spiked are switched after 3 hr. An individual response is a bias, i.e., the collaborator's reading minus the true value. Thus, the data framework becomes three responses per collaborator* per level.

Formally, the experimental design model is:

$$X_{ijk} = \mu + C_i + L_j + CL_{ij} + e_{k(ij)}$$

where μ = overall mean

C_i = i^{th} collaborator, $i = 1, \dots, 9$

L_j = j^{th} level, $j = 1, \dots, 4$

CL_{ij} = collaborator level interaction

$e_{k(ij)}$ = k^{th} measurement error in ij^{th} cell, $k = 1, \dots, 3$ for every ij^*

X_{ijk} = ijk^{th} bias (collaborator reading - true reading).

* C-1 not included due to anomalous results.

COLLABORATORS' FIELD SAMPLING

The collaborative test took place at the MRI Deramus Field Station during September 23 to 27, 1974. The 10 collaborators (see Figure 12) started the test at 0830, September 23, with an orientation. The NO₂, ambient-air sampling system they used was shown and explained to them. The written instructions that comprise Appendix F were given to and discussed with the collaborators. After this orientation period the collaborators set up their equipment in preparation for the first run. The actual schedule of the four runs that took place is given in Table 1. All 10 collaborators cleared the site by 1900, Friday, September 27.

All collaborators sampled from the spiked line during the A runs. During the B and C runs, the collaborators were divided into two groups with one group sampling on the spiked line while the other group sampled from the unspiked line. At 1250 each day all collaborators then switched sample manifolds--those that had been on spiked went to unspiked and vice versa. Also, the group that was on the spiked line for Run 1-B changed to the unspiked line for 2-B, so that each group began every other B and C run set on the same manifold.

During the test MRI personnel observed that all collaborators followed the sampling procedures given in the method write-up. All collaborators except two determined the nitric oxide start concentration of their span gas cylinder prior to the test at their home laboratories. Two collaborators could not obtain a gas cylinder in time and uncalibrated cylinders were supplied by MRI on the 1st day of the test. These collaborators used an arbitrary nitric oxide concentration during the test and then determined the true value after returning to their home laboratories. Their field data were adjusted accordingly.

Zero and span checks were made by all collaborators during the tests at 0800 and 1630 each day.

The collaborators recorded all pertinent sampling data on their recorder charts. The calculations of the NO₂ levels from the recorder chart readings were made after returning to their home laboratories.



Front Row: Paul Constant,^{a/} Melvin Ken Muir, Jim Harris, Carol Ellis,
Roger Ellard, William Findlay

Back Row: John Higuchi, Bruce DaRos,^{a/} Vinson Thompson, Robert
Richardson, George Scheil,^{a/} Jon Zimmer

^{a/} MRI personnel.

Figure 12. Photograph of field personnel of the NO₂ collaborative test
of the chemiluminescent procedure, MRI Field Station,
September 23 to 27, 1974.

Table 1. COLLABORATIVE TEST SCHEDULE

Level	Run	NO ₂ spike level ($\mu\text{g}/\text{m}^3$)	Date/time	
			Started	Completed
1	A	48.6	9-23-74 at 1800	9-24-74 at 0800
	B	48.6	9-24-74 at 0930	9-24-74 at 1250
	C	48.6	9-24-74 at 1250	9-24-74 at 1630
2	A	186	9-24-74 at 1800	9-25-74 at 0800
	B	186	9-25-74 at 0930	9-25-74 at 1250
	C	186	9-25-74 at 1250	9-25-74 at 1630
3	A	292	9-25-74 at 1800	9-26-74 at 0800
	B	292	9-26-74 at 0930	9-26-74 at 1250
	C	292	9-26-74 at 1250	9-26-74 at 1630
4	A	102	9-26-74 at 1800	9-27-74 at 0800
	B	102	9-27-74 at 0930	9-27-74 at 1250
	C	102	9-27-74 at 1250	9-27-74 at 1630

MRI had a laboratory supervisor who was in charge of the NO₂, ambient-air system operation. He was on duty from 0800 to 1800 each day, which was the period of run starts and completions. He was available anytime during the 24-hr runs, as was the program manager, if any problems arose.

There was a technician on duty throughout each run at all times during the test. These people monitored the sampling system operation, recording operational data and general observations. A general log book was kept as well as log sheets for operational data. Copies of these log sheets are given in Appendix F.

COLLABORATORS' SAMPLING RESULTS

Each collaborator's sampling instrumentation included an analog recorder on which all his sampling data were recorded. Each collaborator calculated 1-hr averages during the A runs and 1/2-hr averages during the B and C runs, from his analog-sampling recordings by a method of his own choosing. These results were submitted to MRI along with his calibration data. The averages of the collaborators are tabularized by NO₂ spiked level* in Tables 2 through 5, with Table 2 comprising Level 1 (48.6 µg/m³ of NO₂) results, Table 3 comprising Level 2 (186 µg/m³ of NO₂) results, Table 4 comprising Level 3 (292 µg/m³ of NO₂) results, and Table 5 comprising Level 4 (102 µg/m³ of NO₂) results. For Runs B and C shown in Tables 2 through 5, two consecutive half-hour average values were averaged arithmetically to provide 1-hr averages. The 1-hr averages were the values used in the statistical analysis.

Each table presents the results of the 10 collaborators for a test day. Explanatory notes are given at the bottom of each table.

MRI checked the collaborators' results for any gross overall error, e.g., misplacement of the decimal point. Minor deviations were attributed to the reading of the analog charts.

The NO₂ sampling system data along with calculated flow rates and spike levels of the system, and data on ambient test conditions are given in Appendix C.

* The level value of NO₂ is that generated by the permeation tubes.

Table 2. AVERAGE RESULTS OF COLLABORATORS FROM THEIR SAMPLING NO₂ AT LEVEL 1 (48.6 µg/m³)^{a/}

Run	Date	Time	Collaborators									
			A	B	C	D	E	F ^{b/}	G	H	I	J
A	9-23-74	1800-1900	56	61	64	84	60	156	56	56	51	51
	9-23-74	1900-2000	66	66	75	90	66	165	64	68	54	54
	9-23-74	2000-2100	94	103	105	111	90	242	98	98	79	88
	9-23-74	2100-2200	113	117	115	126	100	274	115	109	88	100
	9-23-74	2200-2300	94	84	81	100	73	192	79	75	62	64
	9-23-74	2300-2400	66	70	75	90	68	175	66	70	54	60
	9-24-74	2400-1000	66	66	70	88	58	158	60	56	49	60
	9-24-74	0100-0200	66	66	68	86	60	162	62	58	49	60
	9-24-74	0200-0300	66	70	68	88	64	160	68	62	51	56
	9-24-74	0300-0400	66	66	68	81	54	154	58	56	47	54
	9-24-74	0400-0500	66	61	68	79	58	154	56	56	47	54
	9-24-74	0500-0600	66	66	68	81	62	160	60	56	49	54
	9-24-74	0600-0700	66	70	68	83	64	171	66	58	53	54
	9-24-74	0700-0800	75	80	79	90	70	188	73	73	60	60
B	9-24-74	0930-1000	95d/	145d/	85d/	435d/	245d/	171d/	66d/	56d/	-	54d/
	9-24-74	1000-1030	95/	95/	115/	395/	195/	156	62	49	53	51
	9-24-74	1030-1100	05/	55/	135/	365/	175/	152	60	47	49	51
	9-24-74	1100-1130	05/	55/	175/	385/	155/	148	58	47	47	51
	9-24-74	1130-1200	05/	55/	175/	365/	155/	147	58	47	47	51
	9-24-74	1200-1230	05/	55/	175/	385/	155/	148	60	47	47	51
	9-24-74	1230-1300	05/	55/	175/	385/	155/	150	60	47	47	51
	9-24-74	1300-1330	56	61	58	79	45	245/	95/	05/	65/	05/
	9-24-74	1330-1400	56	61	58	79	53	245/	95/	05/	65/	05/
	9-24-74	1400-1430	56	56	58	79	51	195/	95/	05/	65/	05/
C	9-24-74	1430-1500	56	56	58	79	53	195/	95/	05/	65/	05/
	9-24-74	1500-1530	56	56	58	79	45	195/	95/	05/	65/	05/
	9-24-74	1530-1600	56	61	58	79	51	195/	95/	05/	65/	05/
	9-24-74	1600-1630	56d/	61d/	58d/	79d/	54d/	265d/	95d/	05d/	65d/	05d/

^{a/} This is the spiked value--the statistically determined average true value of NO₂ (which includes ambient NO₂) is 60 µg/m³.

^{b/} F's observations at Level 1 were rejected as outliers.

^{c/} From unspiked samples--all other results are spiked samples.

^{d/} These values are used in the statistical analysis.

Table 3. AVERAGE RESULTS OF COLLABORATORS FROM THEIR SAMPLING NO₂ AT LEVEL 2 (186 µg/m³)^{a/}

Run	Date	Time	Collaborators									
			A	B	C	D	E	F	G	H	I	J
A	9-24-74	1800-1900	197	197	184	165	169	154	195	197	167	-
	9-24-74	1900-2000	197	202	188	169	164	150	195	197	162	177
	9-24-74	2000-2100	197	197	188	167	164	148	194	197	162	177
	9-24-74	2100-2200	197	197	188	165	165	148	194	197	162	177
	9-24-74	2200-2300	197	197	186	165	156	147	192	197	160	177
	9-24-74	2300-2400	197	197	190	165	162	147	195	197	160	177
	9-25-74	2400-0100	197	202	190	167	160	147	194	197	160	177
	9-25-74	0100-0200	197	197	186	165	160	145	188	197	158	177
	9-25-74	0200-0300	197	197	186	167	156	145	188	197	158	177
	9-25-74	0300-0400	197	197	188	165	160	147	192	197	158	177
	9-25-74	0400-0500	197	197	186	162	156	145	188	197	158	177
	9-25-74	0500-0600	197	202	192	164	162	150	197	201	164	182
	9-25-74	0600-0700	197	202	188	165	156	150	197	199	164	173
	9-25-74	0700-0800	207	207	195	167	158	154	197	207	167	-
B	9-25-74	0930-1000	207 ^{c/}	193 ^{c/}	195 ^{c/}	184 ^{c/}	171 ^{c/}	15 ^{b,c/}	15 ^{b,c/}	9 ^{b,c/}	15 ^{b,c/}	6 ^{b,c/}
	9-25-74	1000-1030	216	197	205	178	188	13 ^{b/}	19 ^{b/}	15 ^{b/}	17 ^{b/}	6 ^{b/}
	9-25-74	1030-1100	216	202	205	190	180	15 ^{b/}	24 ^{b/}	19 ^{b/}	19 ^{b/}	6 ^{b/}
	9-25-74	1100-1130	216	202	201	190	180	13 ^{b/}	24 ^{b/}	19 ^{b/}	19 ^{b/}	9 ^{b/}
	9-25-74	1130-1200	216	202	201	180	180	13 ^{b/}	22 ^{b/}	19 ^{b/}	19 ^{b/}	17 ^{b/}
	9-25-74	1200-1230	216	197	199	177	182	13 ^{b/}	15 ^{b/}	19 ^{b/}	19 ^{b/}	21 ^{b/}
	9-25-74	1230-1300	216	197	205	173	194	15 ^{b/}	24 ^{b/}	19 ^{b/}	21 ^{b/}	21 ^{b/}
	9-25-74	1300-1330	19 ^{b/}	14 ^{b/}	24 ^{b/}	34 ^{b/}	28 ^{b/}	-	199	207	178	194
	9-25-74	1330-1400	9 ^{b/}	9 ^{b/}	17 ^{b/}	30 ^{b/}	28 ^{b/}	-	197	197	169	224
	9-25-74	1400-1430	9 ^{b/}	5 ^{b/}	13 ^{b/}	22 ^{b/}	24 ^{b/}	-	197	197	165	188
C	9-25-74	1430-1500	0 ^{b/}	5 ^{b/}	11 ^{b/}	22 ^{b/}	19 ^{b/}	-	197	197	164	188
	9-25-74	1500-1530	0 ^{b/}	0 ^{b/}	11 ^{b/}	21 ^{b/}	19 ^{b/}	-	197	197	164	188
	9-25-74	1530-1600	0 ^{b/}	0 ^{b/}	11 ^{b/}	21 ^{b/}	19 ^{b/}	-	197	197	164	188
	9-25-74	1600-1630	0 ^{b,c/}	0 ^{b,c/}	11 ^{b,c/}	19 ^{b,c/}	19 ^{b,c/}	-	197 ^{c/}	197 ^{c/}	164	188
											164 ^{c/}	188 ^{c/}
											164 ^{c/}	188 ^{c/}
											164 ^{c/}	188 ^{c/}

^{a/} This is the spiked value--the statistically determined average true value of NO₂ (which includes ambient NO₂) is 203 µg/m³.

^{b/} From unspiked samples--all other results are spiked samples.

^{c/} These values not used in the statistical analysis.

Table 4. AVERAGE RESULTS OF COLLABORATORS FROM THEIR SAMPLING NO₂ AT LEVEL 3 (292 µg/m³)^{a/}

Run	Date	Time	Collaborators									
			A	B	C	D	E	F	G	H	I	J
A	9-25-74	1800-1900	320	-	286	282	258	-	274	318	267	282
	9-25-74	1900-2000	329	-	288	308	244	239	282	320	269	282
	9-25-74	2000-2100	338	310	299	382	254	244	288	327	274	295
	9-25-74	2100-2200	338	310	293	391	248	242	286	325	272	295
	9-25-74	2200-2300	320	296	280	368	246	233	274	312	263	282
	9-25-74	2300-2400	320	296	276	385	242	231	272	308	261	280
	9-26-74	2400-0100	320	296	280	382	231	229	272	306	261	282
	9-26-74	0100-0200	320	291	276	376	244	229	269	301	259	282
	9-26-74	0200-0300	320	291	276	376	254	229	271	301	259	282
	9-26-74	0300-0400	320	291	276	363	254	229	271	303	261	282
	9-26-74	0400-0500	320	291	276	368	254	229	267	301	259	282
	9-26-74	0500-0600	320	291	278	368	254	231	272	301	259	282
	9-26-74	0600-0700	320	296	280	368	256	233	274	308	261	282
	9-26-74	0700-0800	329	301	284	368	258	233	278	316	263	282
B	9-26-74	0930-1000	19 ^{b,c/}	9 ^{b,c/}	21 ^{b,c/}	15 ^{b,c/}	47 ^{b,c/}	32 ^{b,c/}	241 ^{c/}	278 ^{c/}	320 ^{c/}	282 ^{c/}
	9-26-74	1000-1030	9 ^{b/}	9 ^{b/}	19 ^{b/}	17 ^{b/}	47 ^{b/}	28 ^{b/}	239	280	320	295
	9-26-74	1030-1100	9 ^{b/}	9 ^{b/}	17 ^{b/}	13 ^{b/}	47 ^{b/}	28 ^{b/}	237	282	323	295
	9-26-74	1100-1130	9 ^{b/}	5 ^{b/}	17 ^{b/}	11 ^{b/}	43 ^{b/}	28 ^{b/}	237	278	320	295
	9-26-74	1130-1200	9 ^{b/}	5 ^{b/}	13 ^{b/}	11 ^{b/}	43 ^{b/}	22 ^{b/}	235	276	320	295
	9-26-74	1200-1230	9 ^{b/}	0 ^{b/}	11 ^{b/}	8 ^{b/}	36 ^{b/}	19 ^{b/}	233	278	310	295
	9-26-74	1230-1300	0 ^{b/}	0 ^{b/}	11 ^{b/}	8 ^{b/}	38 ^{b/}	13 ^{b/}	235	278	310	295
	9-26-74	1300-1330	320	296	284	258	374	256	19 ^{b/}	9 ^{b/}	0 ^{b/}	28 ^{b/}
	9-26-74	1330-1400	320	296	284	254	357	256	15 ^{b/}	9 ^{b/}	0 ^{b/}	28 ^{b/}
	9-26-74	1400-1430	320	291	280	254	368	259	15 ^{b/}	9 ^{b/}	0 ^{b/}	28 ^{b/}
C	9-26-74	1430-1500	320	291	280	259	338	244	13 ^{b/}	9 ^{b/}	0 ^{b/}	28 ^{b/}
	9-26-74	1500-1530	320	291	280	259	297	259	15 ^{b/}	6 ^{b/}	0 ^{b/}	28 ^{b/}
	9-26-74	1530-1600	320	291	280	258	286	261	15 ^{b/}	8 ^{b/}	0 ^{b/}	28 ^{b/}
	9-26-74	1600-1630	320 ^{c/}	296 ^{c/}	280 ^{c/}	261 ^{c/}	283 ^{c/}	261 ^{c/}	15 ^{b,c/}	9 ^{b,c/}	0 ^{b,c/}	32 ^{b,c/}
	9-26-74	1630-1700	320	296	284	258	374	256	19 ^{b/}	9 ^{b/}	0 ^{b/}	28 ^{b/}
	9-26-74	1700-1730	320	296	284	254	357	256	15 ^{b/}	9 ^{b/}	0 ^{b/}	28 ^{b/}

^{a/} This is the spiked value--the statistically determined average true value of NO₂ (which includes ambient NO₂) is 308 µg/m³.

^{b/} From unspiked samples--all other results are spiked samples.

^{c/} These values not used in the statistical analysis.

Table 5. AVERAGE RESULTS OF COLLABORATORS FROM THEIR SAMPLING NO₂ AT LEVEL 4 (102 µg/m³)^{a/}

Run	Date	Time	Collaborators									
			A	B	C	D	E	F	G	H	I	J
A	9-26-74	1800-1900	94 ^{c/}	84 ^{c/}	88 ^{c/}	113 ^{c/}	103 ^{c/}	81 ^{c/}	86 ^{c/}	92 ^{c/}	94 ^{c/}	103 ^{c/}
	9-26-74	1900-2000	132	117	116	137	107	102	111	118	113	122
	9-26-74	2000-2100	122	108	107	133	102	94	103	103	100	116
	9-26-74	2100-2200	113	108	107	128	94	92	103	103	100	116
	9-26-74	2200-2300	113	103	102	128	90	86	94	103	94	113
	9-26-74	2300-2400	113	103	103	126	92	86	94	103	98	113
	9-27-74	2400-0100	113	103	102	137	83	86	100	-	94	113
	9-27-74	0100-0200	113	99	100	137	83	86	98	-	94	113
	9-27-74	0200-0300	113	99	100	132	86	86	98	90	94	113
	9-27-74	0300-0400	113	103	103	128	94	90	102	92	98	116
	9-27-74	0400-0500	113	103	100	126	88	86	98	94	94	113
	9-27-74	0500-0600	113	99	98	122	90	84	94	94	92	103
	9-27-74	0600-0700	113	99	98	120	88	86	98	94	92	103
	9-27-74	0700-0800	113	103	105	122	94	88	94	94	94	113
B	9-27-74	0930-1000	113 ^{c/}	94 ^{c/}	100 ^{c/}	103 ^{c/}	86 ^{c/}	8 ^{b,c/}	4 ^{b,c/}	-	9 ^{b,c/}	6 ^{b,c/}
	9-27-74	1000-1030	103	94	100	103	88	6 ^{b/}	0 ^{b/}	-	8 ^{b/}	6 ^{b/}
	9-27-74	1030-1100	113	103	102	109	81	9 ^{b/}	4 ^{b/}	-	9 ^{b/}	8 ^{b/}
	9-27-74	1100-1130	122	108	111	115	92	15 ^{b/}	9 ^{b/}	-	19 ^{b/}	8 ^{b/}
	9-27-74	1130-1200	113	103	102	107	94	6 ^{b/}	2 ^{b/}	-	9 ^{b/}	9 ^{b/}
	9-27-74	1200-1230	113	103	102	109	92	6 ^{b/}	2 ^{b/}	-	8 ^{b/}	9 ^{b/}
	9-27-74	1230-1300	113	103	100	103	96	6 ^{b/}	0 ^{b/}	-	8 ^{b/}	9 ^{b/}
	9-27-74	1300-1330	0 ^{b/}	0 ^{b/}	11 ^{b/}	28 ^{b/}	19 ^{b/}	84	98	-	96	102
	9-27-74	1330-1400	0 ^{b/}	0 ^{b/}	11 ^{b/}	28 ^{b/}	21 ^{b/}	84	96	-	96	105
	9-27-74	1400-1430	0 ^{b/}	0 ^{b/}	11 ^{b/}	30 ^{b/}	21 ^{b/}	86	100	-	96	105
C	9-27-74	1430-1500	0 ^{b/}	0 ^{b/}	11 ^{b/}	28 ^{b/}	22 ^{b/}	84	102	-	98	105
	9-27-74	1500-1530	0 ^{b/}	5 ^{b/}	8 ^{b/}	24 ^{b/}	17 ^{b/}	84	100	-	96	105
	9-27-74	1530-1600	0 ^{b/}	5 ^{b/}	11 ^{b/}	28 ^{b/}	17 ^{b/}	86	100	-	96	105
	9-27-74	1600-1630	0 ^{b,c/}	5 ^{b,c/}	11 ^{b,c/}	28 ^{b,c/}	19 ^{b,c/}	86 ^{c/}	102 ^{c/}	-	96 ^{c/}	107 ^{c/}
	9-27-74											
	9-27-74											

^{a/} This is the spiked value--the statistically determined average true value of NO₂ (which includes ambient NO₂) is 113 µg/m³.

^{b/} From unspiked samples--all other results are spiked samples.

^{c/} These values not used in the statistical analysis.

STATISTICAL ANALYSIS OF COLLABORATORS' RESULTS

The analysis of the spiked readings and the analysis of the ambient readings will be discussed separately. A summary discussion will follow.

ANALYSIS OF ALL SPIKED READINGS

Recall that the experimental design model for this set is:

$$X_{ijl\ell} = \mu + C_i + t_j + L_k + e_{\ell(ijk)}$$

where μ = overall mean

C_i = i^{th} collaborator, $i = 1, \dots, 10$

t_j = j^{th} hour, $j = 1, \dots, 20$

L_k = k^{th} NO_2 level, $k = 1, \dots, 4$

$e_{\ell(ijk)}$ = measurement error in ℓ^{th} reading in ijk^{th} cell, $\ell = 1$ for every ijk

X_{ijkl} = $ijkl^{\text{th}}$ response (spiked reading).

The results of the analysis of variance of the spiked readings are shown in Tables 6 through 8.

Table 6 shows the basic analyses of variance themselves. Note that a separate analysis of variance was done for each level. This was necessary because the variability within a collaborator (described by σ_e) was not the same at all NO_2 levels (see also Table 9).*

* An assumption (the homoscedastic assumption) of all analysis of variance models is that σ_e is uniform.

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Table 6. ANALYSES OF VARIANCE, SPIKED READINGS ($\mu\text{g}/\text{m}^3$)

<u>Source</u>	<u>df</u>	<u>SS</u>	<u>MS</u>	<u>F</u>
<u>Level 1</u> *				
Total		674,178		
Collaborators, adjusted	8	10,723	1,340	121+
Time (t), adjusted	13	24,868	1,913	173+
Error (e)	104	1,147	11.03	
<u>Level 2</u>				
Total	165	5,483,037		
C, adjusted	9	47,869	5,319	369+
t, adjusted	19	3,858	203	14.1
e	135	1,945	14.41	
<u>Level 3</u>				
Total	167	14,038,750		
C, adjusted	9	227,039	25,227	68.71
t, adjusted	19	11,194	589	1.60
e	137	50,302	367.17	
<u>Level 4</u>				
Total	155	1,677,020		
C, adjusted	9	17,687	1,965	133+
t, adjusted	19	3,446	181	10.5
e	115	1,987	17.28	

* Collaborator F deleted as an outlier at level 1.

Table 7. COLLABORATOR AVERAGE ESTIMATES* SPIKED READINGS ($\mu\text{g}/\text{m}^3$)

Collaborator	Level 1 (avg 79)	Level 2 (avg 181)	Level 3 (avg 287)	Level 4 (avg 103)
A	70	199	330	115
B	72	197	303	104
C	73	189	289	103
D	89	166	366	125
E	65	162	258	91
F	174**	149	225	88
G	68	193	280	99
H	64	197	316	98
I	55	161	269	96
J	60	180	290	111

* The sample averages per level per collaborator are not unbiased estimates of the true collaborator means, because a collaborator missed some hours during a day. The sample average differences between collaborators are not unbiased estimates of the true collaborator differences because different collaborators missed different hours. The values shown in the table are the unbiased estimates (produced by the general analysis of variances).

** Not included in the analyses of variance.

Table 8. COLLABORATOR RANK ORDERS (ASCENDING) PER NO₂ LEVEL

Collaborator	L1	L2	L3	L4
F	10	1	1	1
A	6	10	9	9
B	7	8	7	7
G	5	7	4	5
H	3	9	8	4
C	4	6	5	6
I	1	2	3	3
D	9	4	10	10
E	4	3	2	2
J	2	5	6	8

Table 9. COMPONENTS OF VARIANCE, SPIKED READINGS (pg/m³)

Source	Level 1 (avg. 79)	Level 2 (avg. 181)	Level 3 (avg. 287)	Level 4 (avg. 103)	Average (avg. 163)
σ_e	3.32	3.80	19.16	4.16	10.12
σ_c	9.74	16.29	35.26	9.87	20.62
σ_t	14.54	4.34	4.71	4.05	8.20
$\sqrt{\frac{\sigma_e^2 + \sigma_c^2}{2}}$	10.29	16.73	40.13	10.71	22.97

All the F-values in Table 6 are significant, i.e., at all levels of NO_2 the collaborator averages are separated and a significant variability in NO_2 exists in time.

Since the C and t effects are significant, it is desirable to quantitatively describe the differences between collaborators. Table 7 displays the averages for each NO_2 level. The average NO_2 value per level is listed in this table in order to give a rough idea of the relative separation of collaborators (even though the average value is not a "true").

Since the collaborator (mean) differences are often quite large, at least some of the collaborators must be biased significantly. Note that Collaborator F produced a very strange reading at Level 1, and was rejected as an outlier (despite the fact that the true NO_2 values are unknown). Collaborator F was not deleted from the other NO_2 levels.

Also, the order of the collaborators seems to vary quite a bit from level to level. The Kendall concordance (a coefficient of agreement equal to one when order is perfectly preserved) is only 0.53. Therefore, it is reasonable to suppose that a significant collaborator-level interaction exists (see Figure 13).

The components of variance are shown in Table 9. Recall that:

σ_e = standard deviation within a collaborator,

σ_c = standard deviation between collaborator means,

σ_t = standard deviation between hourly means.

Although we do not know the exact NO_2 values per level, it is surely true that in descending order the levels are L4, L1, L3, L2; approximately spanning the range 80 to 300 $\mu\text{g}/\text{m}^3$. Therefore, Table 9 indicates that σ_c is proportional to the NO_2 level. The σ_e component varies with the NO_2 level, but not in a simple way.

Also, σ_c is larger than σ_e ; i.e., the variability between collaborators is greater than the variability within a collaborator.

As a point of interest, note that σ_t also varies but is not proportional to the NO_2 level; that is, the ambient fluctuations were not consistent from day to day.

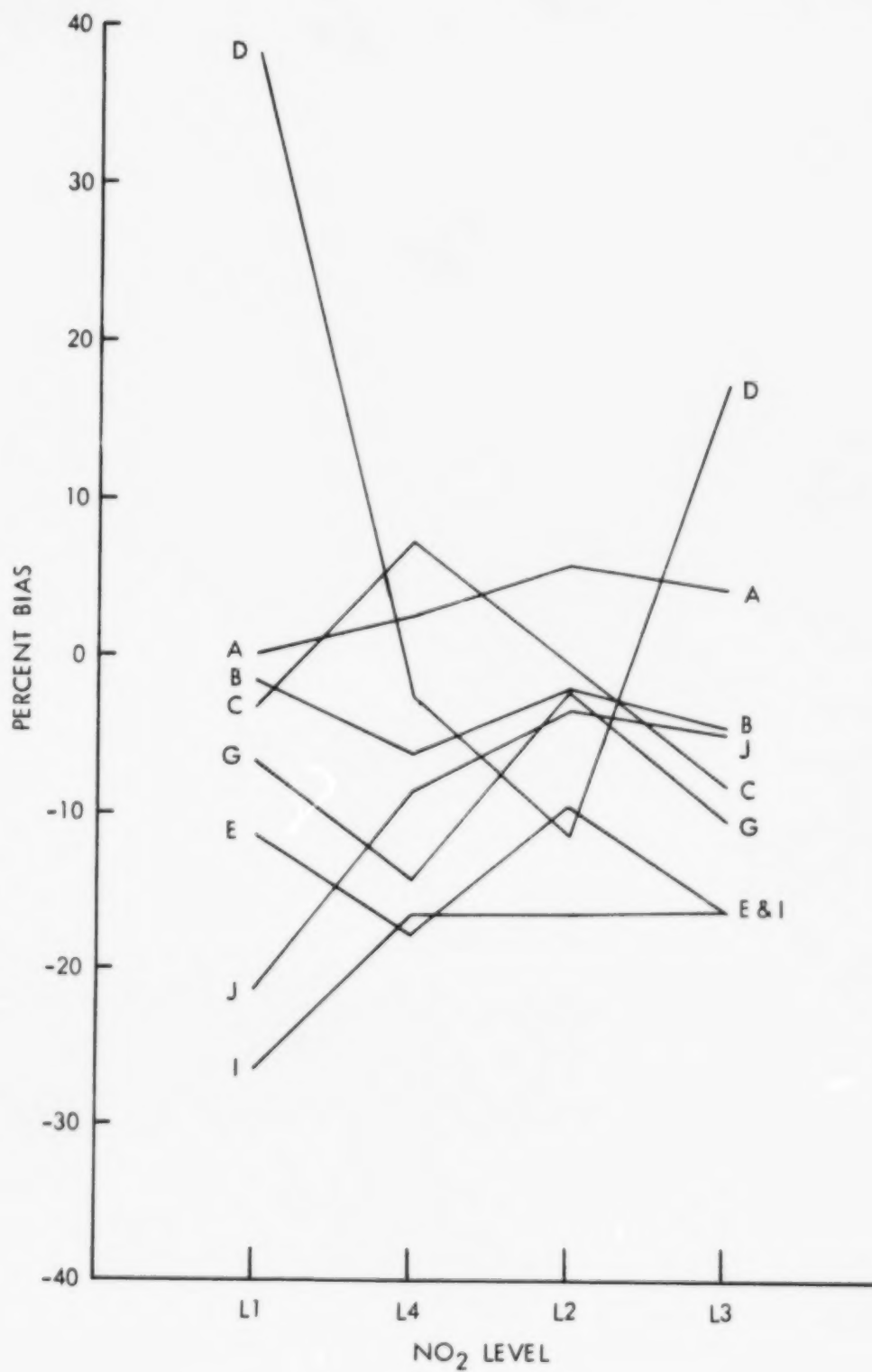


Figure 13. Collaborator-level interaction.

ANALYSIS OF SPIKED AMBIENT READINGS

The experimental design model for this data set is:

$$X_{ijk} = \mu + C_i + L_j + CL_{ij} + e_{k(ij)}$$

where μ = overall mean

C_i = i^{th} collaborator, $C = 1, \dots, 9^*$

L_j = j^{th} NO_2 level, $i = 1, \dots, 4$

CL_{ij} = collaborator level interaction

$e_{k(ij)}$ = k^{th} measurement error in ij^{th} cell, $k = 1, \dots, 3$ for every ij

X_{ijk} = ijk^{th} bias (collaborator reading - true value).

Recall that a true value for each hour is constructed from the average ambient observation during that hour. Since only half the collaborators were measuring the ambient at a given time, their average value has this source of error in it.

The analysis of variance is shown in Table 10. All the F-values in Table 10 are highly significant. Therefore, the bias does differ between collaborators, does depend on the NO_2 level, and the individual collaborator's bias curves are not parallel.

The biases of Collaborator F varied from -24% to +125% at various NO_2 levels. These values are far larger than those exhibited by any other collaborator, so Collaborator F was deleted from the analysis.

This complicated situation is displayed in Figure 13 and Table 11.

The overall average bias is $-8 \mu\text{g}/\text{m}^3$, or about -5%. The absolute bias is the most at the highest NO_2 level, but the percentage bias is most at the lower NO_2 levels.

Although the CL interaction term is significant, this is mostly due to collaborator D, who exhibited biases ranging from -11 to +38% at various NO_2 levels. In general, the collaborators exhibited fairly stable

* One cell (three observations) was missing; these data were replaced by the usual criteria of minimizing residual sum of squares.

Table 10. ANALYSIS OF VARIANCE BIASES ($\mu\text{g}/\text{m}^3$)

Source	df	SS	MS	F
L	3	1,070.74	356.91	33.58
C	8	18,015.17	2,251.90	211.88
CL	23	19,045.43	828.06	77.91
e	69	733.33	10.63	

Table 11. COLLABORATOR (AVERAGE) BIAS VERSUS NO₂ LEVEL

Collaborator	L1	(60) ^{a/}	L2	(203) ^{a/}	L3	(308) ^{a/}	L4	(113) ^{a/}	Avg	(163) ^{a/}
A	0	(0) ^{b/}	12	(6)	14	(5)	3	(3)	7	(4)
B	-1	(-2)	-4	(-2)	-14	(-5)	-7	(-6)	-7	(-4)
G	-4	(-7)	-4	(-2)	-32	(-10)	-16	(-14)	-14	(-9)
H	-17	(-28)	-3	(-2)	7	(2)	missing		-4	(-2)
C	-2	(-3)	-1	(-1)	-25	(-8)	8	(7)	-5	(-3)
I	-16	(-27)	-34	(-17)	-50	(-16)	-19	(-17)	-30	(-18)
D	23	(38)	-23	(-11)	53	(17)	-3	(-3)	13	(8)
E	-7	(-12)	-20	(-10)	-50	(-16)	-20	(-18)	-24	(-15)
J	-13	(-22)	-7	(-3)	-15	(-5)	-10	(-9)	-11	(-3)
Average	-4	(-7)	-9	(-5)	-12	(-4)	-8	(-7)	-8	(-5)

^{a/} True value in micrograms per cubic meter.^{b/} Numbers in parentheses are percents.

biases over the range of NO_2 examined, and therefore averaging the biases was justified.

SUMMARY DISCUSSION

In general, the measurement error (σ_e) is around 6% and the collaborator variability $\sqrt{\sigma_c^2 + \sigma_e^2}$ about 14% for the NO_2 concentrations examined.

These values (particularly σ_c) do depend on the NO_2 level.

The average bias is low (about -5%), and in general, stable versus NO_2 level. However, one collaborator had very large biases, and another collaborator had unstable biases (as a function of NO_2 level). Nevertheless, it is fair to say that for most collaborators (8 out of 10) using the Chemiluminescent Procedure, the bias is small and well balanced.

In summary then, collaborators using the Chemiluminescent Procedure produce reproducible values with little bias, but the level differences between collaborators are often sizeable.

LOWER DETECTABLE LIMIT (LDL)

Two meanings of LDL are used in the following discussion: (a) the smallest value of NO_2 that can be reliably identified as existing (i.e., positive) when the method is used by a collaborator (a "pure" LDL), and (b) the smallest reliable NO_2 estimate from a set of collaborators using the method (a "practical" LDL).

Two methods of estimating the LDL were used. The first method used was the ambient readings obtained during the actual experiment, while the second method uses the collaborators' calibration curves.*

The ambient readings furnish estimates of σ_e (standard deviation within a collaborator) and σ_c (standard deviation between collaborators) that allow estimation of the LDL's, although there is no way to incorporate bias** into these estimates. Using $\sigma_e = 4.69 \mu\text{g}/\text{m}^3$ and $\sigma_c = 6.80 \mu\text{g}/\text{m}^3$, results in:

Estimated pure LDL = $9 \mu\text{g}/\text{m}^3$

Estimated practical LDL = $16 \mu\text{g}/\text{m}^3$.

The calibration curves do allow estimation of biases in addition to components of variance. Using the average S.E. of individual calibration curves results in a pure LDL estimate of $13 \mu\text{g}/\text{m}^3$, of which $5 \mu\text{g}/\text{m}^3$ is bias. Using the whole data set, one arrives at an estimated practical LDL of $22 \mu\text{g}/\text{m}^3$, of which $5 \mu\text{g}/\text{m}^3$ is bias.

The two sets of results agree fairly well. It seems reasonable to state that the pure LDL is probably $\leq 13 \mu\text{g}/\text{m}^3$, and the practical LDL $\leq 22 \mu\text{g}/\text{m}^3$.

* The only calibration data available were from Collaborators B and H.

** The intercept on the calibration curve.

CONCLUSIONS

The major conclusions that can be drawn from the results of this collaborative test are:

1. The NO₂, ambient-air sampling system developed by MRI is an effective system for use in collaborative testing of manual and instrumental methods such as those tested on this program.

2. The "Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere (Chemiluminescent Procedure)" is adequately written for those knowledgeable in sampling and analysis techniques as presented therein.

3. If the tentative Chemiluminescent Procedure as given in Appendix A of this report is followed by people knowledgeable in the sampling and analysis techniques given therein, then such persons will obtain results with an average bias of -8 µg/m³ over the range 80 to 300 µg/m³. On the average, the within laboratory standard deviation (σ_e) is 6%, and the collaborative standard deviation $\sqrt{\sigma_c^2 + \sigma_e^2}$ is 14%. These components are dependent, however, upon the NO₂ level.

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RECOMMENDATIONS

Based upon the conclusions that have been drawn from the results of this collaborative test, it is recommended that no further collaborative testing and analysis be done on any of the four methods tested--sodium-arsenite, TGS-ANSA, continuous colorimetric and chemiluminescent.

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APPENDIX A

TENTATIVE METHOD FOR THE CONTINUOUS MEASUREMENT OF
NITROGEN DIOXIDE IN THE ATMOSPHERE
(CHEMILUMINESCENT PROCEDURE)

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TENTATIVE METHOD FOR THE CONTINUOUS MEASUREMENT OF
NITROGEN DIOXIDE IN THE ATMOSPHERE (CHEMILUMINESCENT PROCEDURE)^a

^aA tentative method is one which has been carefully drafted from available experimental information, reviewed editorially within the Methods Standardization and Performance Evaluation Branch/QAEP/L, and has undergone extensive laboratory evaluation. The method is still under investigation and, therefore, is subject to revision.

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1. Principle and Applicability

1.1 Atmospheric concentrations of nitrogen dioxide (NO_2) are measured indirectly by the chemiluminescent reaction of nitric oxide (NO) with ozone (O_3) at reduced or near atmospheric pressures. (1,2,3,4) NO_2 is first thermally converted⁽⁵⁾ (reduced) to NO before it is reacted with O_3 . A photomultiplier tube detector measures the intensity of the light from the resulting chemiluminescent reaction. Since ambient air usually contains both NO_2 and NO simultaneously, some means must be provided for distinguishing between the NO concentration already in the sample and the NO concentration resulting from the reduction of NO_2 to NO. Ambient air is drawn directly into the detector assembly to determine the NO concentration. The NO_x concentration ($\text{NO} + \text{NO}_2$) is measured when the air is passed through the thermal converter and then into the detector. The NO_2 concentration is then determined electronically by subtracting the NO detector response (or concentration) from the NO_x detector response. The measurement is accomplished in approximately one minute.

1.2 The procedure is applicable to the continuous measurement of NO_2 in ambient air.

2. Range and Lower Detectable Limit

2.1 Analyzers with full scale ranges from 0 to $376 \text{ } \mu\text{g}/\text{m}^3$ (0 to 0.2 ppm) to 0 to $18,800 \text{ } \mu\text{g}/\text{m}^3$ NO_2 (0 to 10 ppm) are available. The full scale NO_2 range recommended for normal ambient air

measurements is the most sensitive range on the analyzer not to exceed a sensitivity of 0 to 940 $\mu\text{g}/\text{m}^3$ (0 to 0.5 ppm). Separate range selectors should be made available for NO, NO₂ and NO_x since NO_x concentrations sometimes exceed 1 ppm.

2.2 The lower detectable limit is approximately 20 $\mu\text{g}/\text{m}^3$ (0.01 ppm) at the 0 to 940 $\mu\text{g}/\text{m}^3$ (0-0.5 ppm) range.

3. Interferences

3.1 The chemiluminescent detection of NO with O₃ is not subject to interference from any of the common air pollutants such as O₃, NO₂, CO, NH₃ and SO₂.⁽¹⁾ The elimination of possible hydrocarbon interference is achieved by means of a red sharp-cut optical filter.

3.2 Any compounds which will be converted to NO in the thermal converter will interfere with the measurement of the NO_x (NO + NO₂) concentration. The principal compound of concern is ammonia; however, it is not an interferent at converter temperatures below 300° C. Unstable nitrogen compounds, such as peroxyacetylnitrate (PAN) and organic nitrites decompose thermally to form NO. However, their ambient concentrations are usually so low that their interference can be disregarded.

4. Apparatus

4.1 Nitrogen Dioxide Analyzer. The analyzer should be of the chemiluminescent type with a linear response over the desired

range. The analyzer should meet or exceed the specifications described in Appendix A. See Figure 1 for a general schematic of a typical chemiluminescent analyzer.

5. Procedure

5.1 Ambient air is drawn into the analyzer with a sample pump or with the vacuum pump used in the detector. Ozonized oxygen or air at a constant flow is drawn into the detector assembly to react with the sample. For exact operating procedures refer to the analyzer instruction manual.

6. Calibration

6.1 Principle. The calibration technique is based upon application of the rapid gas phase reaction between NO and O₃ to produce a stoichiometric quantity of NO₂.^(2,3)



The quantitative nature of the reaction is used in a manner such that, once the concentration of one component is specified, the concentrations of the other two are determined. The stoichiometry of the reaction holds only when NO is present in excess.

Atmospheres of known O₃ concentration are produced from an ozone generator, the output of which has been calibrated by iodometry (neutral buffered KI procedure).⁽⁶⁾ The NO content of an NO in N₂ cylinder (50-100 ppm) is then assayed by gas phase

titration with the O_3 . Analysis of the NO cylinder is necessary because the nominal NO concentration of some manufacturers has been found to be inaccurate. The amount of O_3 added in the titration is equivalent to the amount of NO consumed (or NO_2 produced), thus the NO content of the cylinder can be determined.

Once the cylinder is assayed it can be used throughout its life to prepare known concentrations of NO. In addition to generating standard NO concentrations for calibrating the NO response of an analyzer, the assayed NO cylinder is also used to generate known NO_2 concentrations by a gas phase titration with O_3 . To calibrate the NO_2 response of a chemiluminescent analyzer, O_3 is added in increments to excess NO. The incremental decrease in NO concentration (observed by noting the NO detector response of the analyzer) is equivalent to the NO_2 produced in the titration. Since the NO_2 is produced continually in the titration, a dynamic calibration results.

6.2 Apparatus. A schematic drawing of the gas phase titration apparatus is shown in Figure 2.

6.2.1 Pressure regulator for NO cylinder. A regulator to fit the NO cylinder having internal parts of stainless steel with a Teflon or Kel-F seat and a delivery pressure of 30 psi. Note: This regulator as well as needle valve and delivery lines should be thoroughly flushed after connecting to the NO cylinder. Flushing can be accomplished by adjusting the delivery pressure to near maximum and venting the gas for several minutes.

6.2.2 Needle valves. Stainless steel parts are required in controlling the NO flow. Component parts are not critical for control of air flow.

6.2.3 Flowmeters

6.2.3.1 NO flow. A flowmeter capable of monitoring NO flows between 0-100 cm³/min. A 25 cm³ capacity soap bubble flowmeter is required for measuring absolute NO flows.

6.2.3.2 Air flow. A flowmeter capable of monitoring flows between 0 and 10 l/min. A large soap bubble meter or wet test meter is required for calibration of the flow meter and for making absolute flow measurements in this range.

6.2.4 Capillary restrictor. Glass or stainless steel capillary of the proper I.D. and length to maintain a 1:10 to 1:15 ratio of air flow through the generator to total air flow. A Teflon or stainless steel needle valve can be used in place of a capillary restrictor provided that a stable flow through the generator is maintained.

6.2.5 Calibrated Ozone Generator. Capable of producing O₃ over the range 0 to 1 ppm at a total air flow rate of 2 to 10 l/min. One such ozone source consists of a quartz tube into which ozone-free air is introduced and then irradiated with a stable low-pressure mercury lamp.^(7,8) The lamp's level of irradiation is controlled by an adjustable aluminum sleeve which fits around the lamp. Ozone concentrations are varied by adjustment of this sleeve. At a fixed level of air flow and irradiation, ozone is produced at a constant rate.

6.2.6 Reaction Chamber and Mixing Bulb. Kjeldahl connecting bulbs with volumes of approximately 250 cm^3 should be used.

6.2.7 Sample Manifold. A multiport all-glass manifold should be used. All connections in the calibration system should be glass or Teflon.

6.3 Reagents **

6.3.1 Nitric Oxide. Cylinder containing approximately 50 to 100 ppm NO in N_2 with less than 1 ppm NO_2 . In ordering cylinders from commercial vendors, specify the use of O_2 free N_2 . This will minimize NO_2 formation.

6.3.2 Clean Air Source. Compressed (house) or cylinder air containing no more than 0.005 ppm of NO, NO_2 , and O_3 , or reactive hydrocarbons. The air is cleaned by passing it through silica gel for drying, treating with ozone to convert any NO to NO_2 , and finally by passing through activated charcoal (6-14 mesh), and molecular sieve (6-16 mesh, type 4A), to remove any NO_2 or hydrocarbons. Regardless of the source of air, compressed (house) or cylinder air, it should be purified as described above.

6.4 Procedure. The gas phase titration apparatus shown in Figure 2 is used to assay the NO cylinder and also to generate NO_2 for analyzer calibration. NO from the cylinder is diluted with a constant flow of clean air (with the ozone source set at zero O_3 concentration) to produce an NO concentration at the sample manifold of approximately 1 ppm. The ozone source is then adjusted to produce

incremental increases in O_3 concentration which result in equivalent incremental decreases in NO concentration down to approximately 0.05 ppm NO. During this titration NO_2 is generated in amounts equivalent to the NO consumed by the O_3 .

Upstream of the ozone generator, the air stream is split such that the capillary restrictor allows only 1/10 to 1/15 of the total air flow to go through the ozone generator, with the remainder bypassing the generator. The air stream is split in order to permit low flows through the ozone generator to create locally high concentrations of O_3 and NO in the reaction chamber. At these high concentrations and low flows, the reaction chamber provides a residence time long enough for quantitative reaction to occur. The NO- NO_2 mixture is combined with the bypassed air in the mixing chamber. The turbulent flow created assures a homogeneous sample at the sample manifold.

6.4.1 Analysis of NO cylinder by Gas Phase Titration (G.P.T.). Allow the chemiluminescent analyzer to sample clean air until a stable response is obtained. After the response has stabilized, make proper zero adjustment. Determine the NO concentration in the cylinder as follows. With the NO flow off, set the clean air flow at approximately 2 to 10 L/min. (the actual flow depends on the operating characteristics of the ozone generator, Section 6.2.5). Measure and record the absolute air flow, F_0 . Adjust the NO flow to generate approximately 1.0 ppm NO at the manifold. (Use the NO cylinder concentration provided by the manufacturer.) Measure and record the absolute NO flow, F_{NO} . Adjust the span control for NO response on a 0 to 1 ppm range so

that the NO response reads exactly the NO concentration generated. After the NO response has stabilized, record the reading and then add approximately 0.1 ppm O₃ by adjustment of the calibrated ozone source. (The ozone source should be stable before beginning the gas phase titration.) Allow the NO response to stabilize and record the reading. (Readings may be taken directly from the instrument readout or from a properly spanned recorder.) Adjust the ozone source to obtain approximately 0.2 ppm O₃ and allow the NO response to stabilize. Continue this procedure until up to 0.8 to 1.0 ppm O₃ has been added in a stepwise fashion. A minimum of six ozone additions are required. Remeasure F_O and F_{NO} to insure that the flows have not changed during the titration.

6.4.1.1 Calculation. Plot the O₃ concentration added (y-axis) versus the resultant NO concentration in ppm (x-axis). A linear curve should be obtained. (See Figure 3, for example.) The O₃ concentration at the y-axis intercept, C'_O, is the O₃ equivalent to the initial diluted NO concentration. The cylinder NO concentration is calculated as follows:

$$C_{NO} = \frac{F_O \times C'_O}{F_{NO}}$$

where C_{NO} = cylinder NO concentration, ppm

F_{NO} = measured NO flow, cm³/min.

C'_O = O₃ equivalence point, ppm

F_O = total clean air flow, cm³/min.

6.4.2 NO₂ Impurity in the NO Cylinder. The concentration of NO₂ in the NO cylinder must be determined because the error in disregarding this impurity can be significant. Consider, for example, a 100 ppm NO cylinder with only 1 ppm of NO₂. When used to generate 1 ppm NO for G.P.T., the NO₂ is diluted to 0.01 ppm. Although this is a small amount of NO₂, the error it would introduce relative to typical measured NO₂ concentrations, 0.03 to 0.05 ppm, would be greater than 20%. The NO₂ impurity in the cylinder must be determined by an independent method which has no appreciable interference from NO. The triethanolamine-quaiacol-sulfite (TGS) manual method⁽⁹⁾ is recommended. However, any other method which measures NO₂ directly and has no interference from NO may be used.

To determine the amount of NO₂ impurity in the NO cylinder, sample a diluted stream from the cylinder. The exact dilution will depend on the NO₂ concentration in the cylinder and the method chosen for analysis. Generally, dilutions of 1 to 100 or 1 to 50 will be adequate. Convert the NO₂ analyzed to ppm. Then calculate the NO₂ impurity using:

$$C_{\text{NO}_2} = \frac{(\text{NO}_2)_A \times F_T}{F_{\text{NO}}}$$

where C_{NO_2} = NO₂ concentration in cylinder, ppm

$(\text{NO}_2)_A$ = NO₂ concentration analyzed, ppm

F_T = Total flow at manifold, cm³/min.

F_{NO} = Flow from NO cylinder, cm³/min.

6.4.3 NO_2 Converter Efficiency. The efficiency of the NO_2 converter should be constant and linear over the range of operation. The NO_2 converter efficiency may be determined in the following manner. While the chemiluminescent analyzer is sampling clean air, adjust the zero controls for the NO and NO_x responses to read zero. Dilute the assayed cylinder of NO with clean air to produce approximately 1.0 ppm NO and adjust the span controls for the NO and NO_x responses to read exactly the NO concentration generated. The exact NO concentration is calculated as follows:

$$(\text{NO}) = \frac{F_{\text{NO}} \times C_{\text{NO}}}{F_T}$$

where (NO) = NO concentration generated, ppm

C_{NO} = cylinder NO concentration, ppm

F_{NO} = NO flow, cm^3/min

F_T = total flow at manifold, cm^3/min

Note: If NO_2 impurity is present in the NO cylinder, adjust the span control for NO_x response to include the NO_2 impurity concentration assuming a converter efficiency of 1.

Observe and record the initial NO and NO_x readings. Next, add ozone to the NO stream to reduce the NO response to 0.9 ppm. Observe and record the final NO and NO_x readings. Repeat the above procedure adding ozone such that the NO response is decreased to 0.8,

0.7, 0.6 and 0.5 ppm successively. Calculate the concentration of NO_2 generated by G.P.T. for each stepwise addition of ozone, the total NO_2 concentration generated, and the concentration of NO_2 converted to NO as follows:

$$\text{NO}_2 \text{ G.P.T., ppm} = \text{NO}_{\text{Initial, ppm}} - \text{NO}_{\text{Final, ppm}}$$

$$\text{NO}_2 \text{ Generated, ppm} = \text{NO}_2 \text{ G.P.T., ppm} + \text{NO}_2 \text{ Impurity, ppm}$$

$$\text{NO}_2 \text{ Converted, ppm} = \text{NO}_x \text{ Final, ppm} - \text{NO}_{\text{Final, ppm}}$$

Plot the NO_2 concentration converted (y-axis) versus the total NO_2 concentration generated (x-axis). The slope of this plot is the converter efficiency. A straight line indicates a constant converter efficiency over the 0 to 0.5 ppm range. If the converter efficiency is less than 0.90 (90%) or if it is not constant (i.e. nonlinear curve), the converter should be replaced or rejuvenated.

6.4.3.1 Frequency of Determination. The converter efficiency should be determined monthly when the instrument calibration is checked (Section 6.4.4.2).

6.4.4 NO_2 Calibration (0 to 0.5 ppm range).

6.4.4.1 Procedure. While sampling zero air from the gas phase titration apparatus, zero the NO, NO_x and NO_2 detector responses. Adjust the NO flow rate to generate approximately 1.0 ppm NO by

flow dilution (Section 6.4.3) and adjust the span controls to read the exact NO concentration generated. Any NO₂ impurity in the NO cylinder should be included (with an appropriate correction for dilution and converter efficiency) in the NO_x span adjustment.

Adjust the ozone source to add enough O₃ to decrease the NO response to approximately 0.50 ppm. This results in the generation of an equivalent amount of NO₂ which is used to span the NO₂ response. Allow the response of the instrument to stabilize and adjust the span control to give a direct readout of the generated NO₂, including any NO₂ impurity if present. Continue to decrease the O₃ concentration so as to produce NO₂ concentrations of approximately 0.40, 0.20, 0.10 and 0.05 ppm. Using this procedure the NO₂ generated can be determined by the following equation:

$$\text{NO}_2 \text{ Generated} = \text{NO}_{\text{Initial}} - \text{NO}_{\text{Final}} + \text{NO}_2 \text{ Impurity, ppm}$$

where NO₂ Generated = Total concentration of NO₂ generated, ppm

NO_{Initial} = Initial concentration of NO, ppm

NO_{Final} = Concentration of NO after O₃ addition, ppm

Plot the total NO₂ concentration generated versus analyzer NO₂ response. A straight line should be obtained.

6.4.4.2 Frequency of Calibration. A complete calibration should be made once a month. Analyzers should be zeroed and

spanned at 80 ±5% of full scale daily, then adjusted for any drift that is detected. If the drift is more than ±15%, the analyzer should be recalibrated.

7. Calculations

7.1 Determine the NO₂ concentration directly from the NO₂ calibration curve (Section 6.4.4.1).

7.2 Nitrogen dioxide concentrations in ppm can be converted to $\mu\text{g}/\text{m}^3$ at 25° C and 760 mmHg as follows:

$$(\text{NO}_2), \mu\text{g}/\text{m}^3 = (\text{NO}_2), \text{ppm} \times 1880 \times \frac{\mu\text{g}/\text{m}^3}{\text{ppm}}$$

8. Bibliography

1. A. Fontijn, A.J. Sabadell, and R.J. Ronco, "Homogeneous Chemiluminescent Measurement of Nitric Oxide with Ozone," Anal. Chem., **42**, 575 (1970).
2. J.A. Hodgeson, R.E. Baumgardner, B.E. Martin, and K.A. Rehme, "Stoichiometry in the Neutral Iodometric Procedure for Ozone by Gas-Phase Titration with Nitric Oxide," Anal. Chem., **43**, 1123 (1971).
3. K.A. Rehme, B.E. Martin, and J.A. Hodgeson, "Tentative Method for the Calibration of Nitric Oxide, Nitrogen Dioxide and Ozone Analyzers by Gas Phase Titration," Environmental Protection Agency, Research Triangle Park, N.C., EPA Publication No. EPA-R2-73-246, March 1974.

4. D.H. Stedman, E.E. Daby, F. Stuhl, and H. Niki, "Analysis of Ozone and Nitric Oxide by a Chemiluminescent Method in Laboratory and Atmospheric Studies of Photochemical Smog," J. Air Poll. Control Assoc., 22, 260 (1972).
5. J.A. Hodgeson, K.A. Rehme, B.E. Martin, and R.K. Stevens, "Measurements for Atmospheric Oxides of Nitrogen and Ammonia by Chemiluminescence," Preprint, Prepared at 1972 APCA Meeting, Miami, Florida, June 1972, Paper No. 72-12.
6. Environmental Protection Agency, "Part 50--National Primary and Secondary Ambient Air Quality Standards," Federal Register, Vol. 36, No. 228, pp. 22384-22397, November 25, 1971.
7. J.A. Hodgeson, R.K. Stevens, and B.E. Martin, "A Stable Ozone Source Applicable as a Secondary Standard for Calibration of Atmospheric Monitors," ISA Transactions, 11, 161 (1972).
8. NBS Technical Note, No. 585, pp. 11-25 (January 1972). Available through: Superintendent of Documents, Government Printing Office, Washington, D.C. 20402. Price 70¢.
9. "An Evaluation of the TGS-ANSA Method for Measurement of NO_2 ," Fuerst, R.G., and J. H. Margeson. Copies of this document, which includes a copy of the method write-up, can be obtained from: Methods Standardization Branch, Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

APPENDIX A

Performance Specifications for Atmospheric-Chemiluminescent- NO₂ Analyzers

<u>Parameter</u>	<u>Unit</u> ^a	<u>Specification</u>
Range ^b	ppm	multiple
Noise	ppm	0-0.005
Lower Detectable Limit	ppm	0.01
Zero Drift, 12-, 24-Hour	ppm	±0.02
Span Drift, 24-Hour	ppm	±0.02
Lag Time	minutes	0.5
Rise Time, 95%	minutes	1.0
Fall Time, 95%	minutes	1.0

^aTo convert from ppm to $\mu\text{g}/\text{m}^3$ at 25° C and 760 mm, multiply by 1880.

^bNo performance test required. All other performance specifications are tested on instrument operating in the 0-0.5 ppm range.

APPENDIX B

Definitions of Performance Specifications

Range - Minimum and maximum concentrations which the system shall be capable of measuring.

Noise - Spontaneous, short duration deviations in the analyzer output about the mean output, which are not caused by input concentration changes.

Lower Detectable Limit - The minimum pollutant concentration which produces a signal of twice the noise level.

Zero Drift - The change in analyzer response to zero pollutant concentration over 12- and 24-hour periods of continuous unadjusted operation.

Span Drift - The change in analyzer response to an upscale pollutant concentration over a 24-hour period of continuous unadjusted operation.

Lag Time - The time interval between a step change in input concentration at the analyzer inlet and the first observable corresponding change in the analyzer response that is equal to twice the noise in the instrument output.

Rise Time - The time interval between initial response and 95% of final response after a step increase in input concentration.

Fall Time - The time interval between initial response and 95% of final response after a step decrease in input concentration.

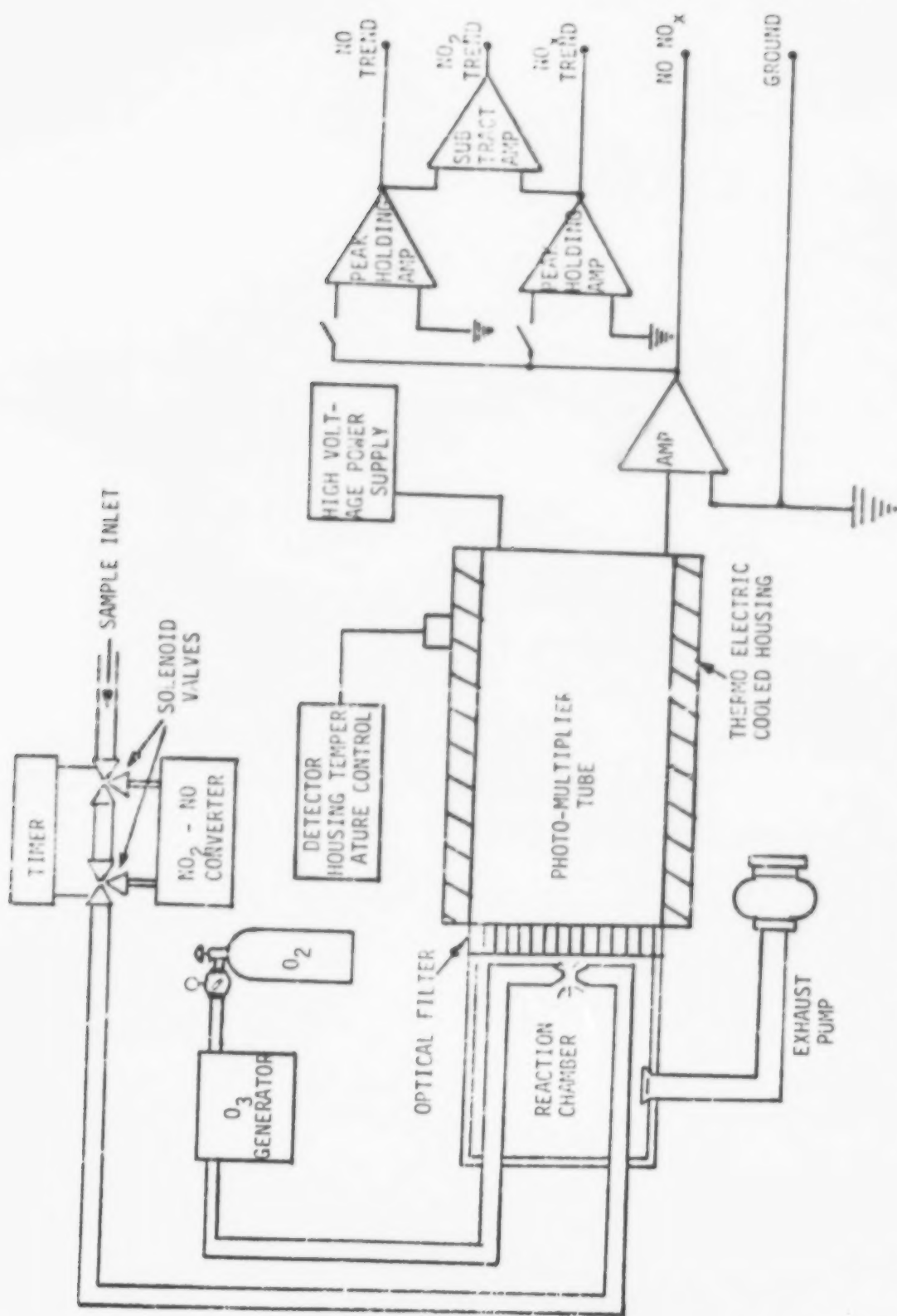


Figure 1. Automated NO, NO₂, NO_x chemiluminescent analyzer.

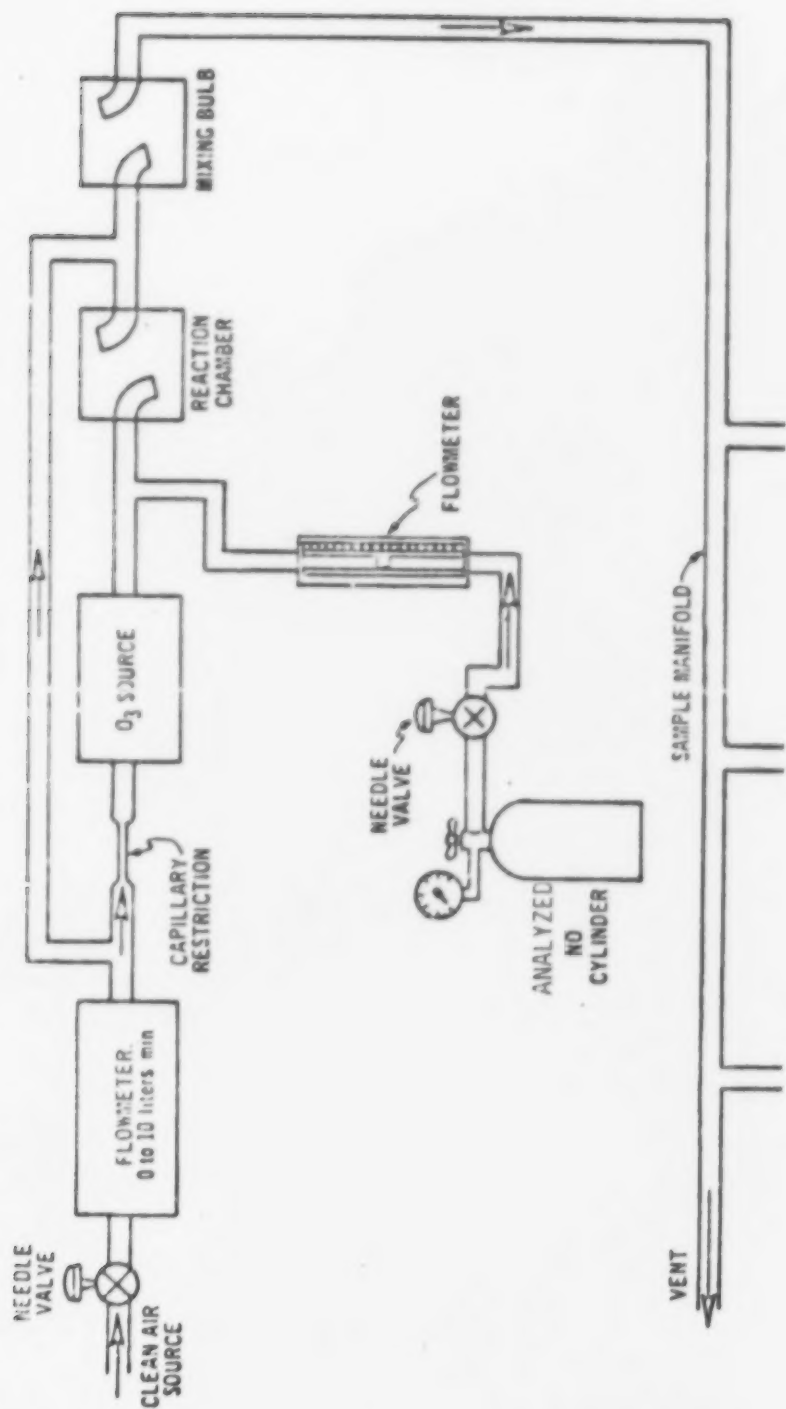


Figure 2. Flow scheme for calibration of NO, NO₂ and NO_x monitor by gas phase titration.

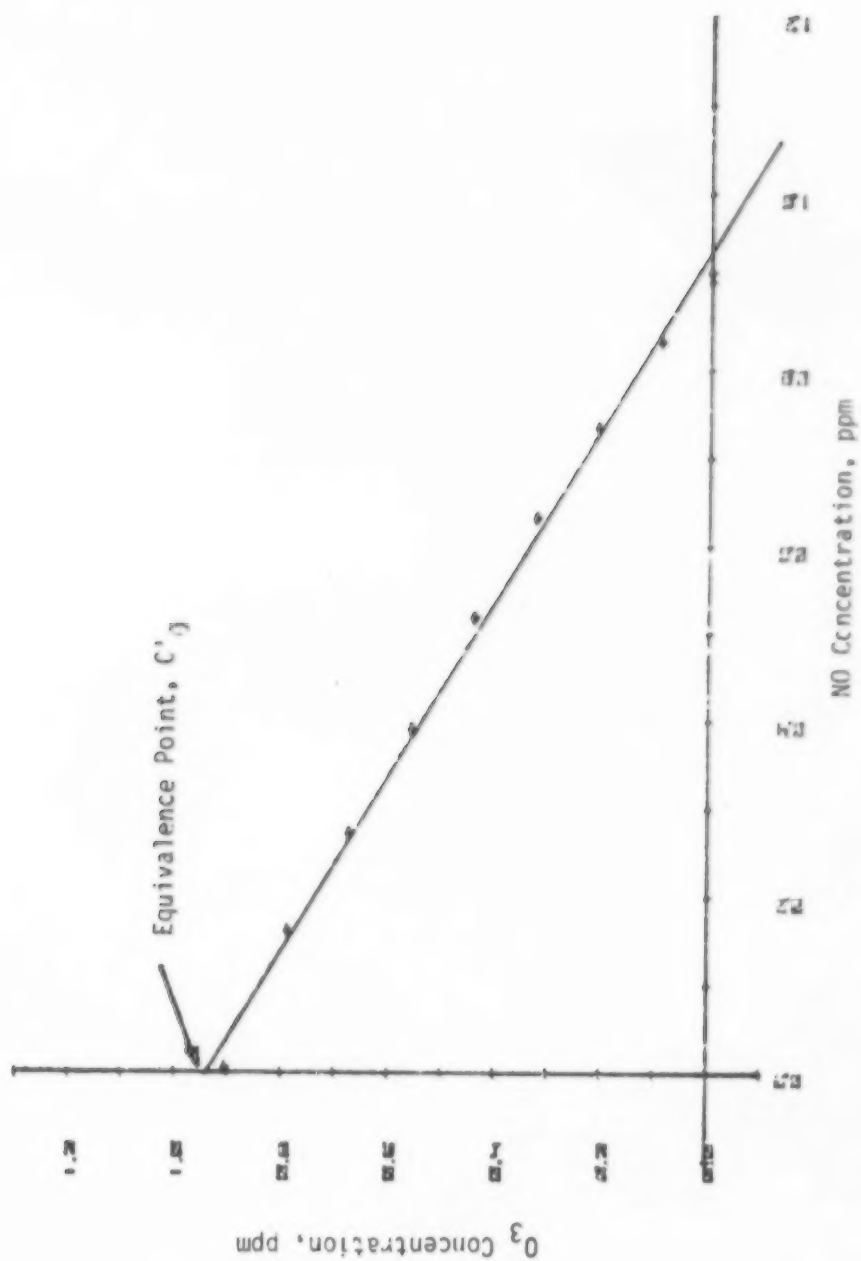


Figure 3. Gas phase titration of NO with O₃.

APPENDIX B

DATA ON THE PERMEATION TUBES USED AS THE
SOURCE OF THE SPIKED LEVELS OF NO₂

There were four branches to the NO₂ permeation tube assembly. Each branch contained a set of permeation tubes as follows:

<u>Branch</u>	<u>Permeation tube</u>		<u>Branch NO₂* ($\mu\text{g}/\text{min}$)²</u>
	<u>Number</u>	<u>Rate of NO₂ ($\mu\text{g}/\text{min}$)</u>	
1	35-8	1.434	-
1	35-16	1.597	-
1	34-7	1.134	-
1	28-10	1.160	-
1			5.325
2	34-3	1.195	-
2	34-13	1.275	-
2	34-6	1.548	-
2	34-1	1.226	-
2	34-10	1.138	-
2			6.382
3	35-13	1.990	-
3	29-4	1.210	-
3			3.200
4	29-2	1.210	-
4	34-12	1.770	-
4			2.980

Permeation rates for the above tubes were determined by the National Bureau of Standards and validated by the Methods Standardization Branch (MSB) of EPA at 25.1°C before they were given to MRI for use on the collaborative test.

The combinations of branches used for the four runs of the chemiluminescent collaborative test are:

<u>Level</u>	<u>Date</u>	<u>Branches used</u>
1	September 23 to 24	4
2	September 24 to 25	1, 3, and 4
3	September 25 to 26	1, 2, 3, and 4
4	September 26 to 27	3 and 4

* The sum of the NO₂ generated by each permeation tube in the branch.

APPENDIX C

CALIBRATION OF THE VENTURI AND DRY-GAS METER

The venturi and dry-gas meter were calibrated using a 1.0-ft³/rev., wet-test meter, as shown in Figure 9 of the text. The wet-test meter is connected between the splitter and the dry-gas meter. A bubbler is used before the wet-test meter to saturate the air with water. The air flow then proceeds through the venturi to the NO₂ bleed-in as it does in normal operation (see Figure 3 of the text).

Since the saturated air coming from the wet-test meter is not dried before going into the dry-gas meter, no correction for water vapor pressure is necessary and only the normal corrections for temperature and pressure are used. The flow rate of the wet-test meter (to stp) is:

$$\text{Flow}_{\text{stp}} = \text{Flow (meter reading)} \times \frac{P}{760} \times \frac{294}{T}$$

where T = temperature of wet-test meter + 273, and
 $P = P_{\text{atm}} + \text{pressure of test meter manometer.}$

The venturi flow rate is dependent on both temperature and pressure. Therefore Flow_{stp} is corrected to venturi conditions.

$$\text{Flow}_{\text{venturi}} = \text{Flow}_{\text{stp}} \times \frac{760}{P_2} \times \frac{T_2}{294}$$

where T_2 = temperature of gas stream + 273, and
 $P_2 = P_{\text{atm}} + P_{\text{(gas stream)}}$

The dry-gas meter is temperature compensated, so only pressure corrections are made for its readings and a temperature base of 21°C is used for calibration. Thus the true flow rate of the dry-gas meter (F_m) is

$$F_m = \text{Flow}_{\text{stp}} \times \frac{760}{P_i}$$

where $P_i = P_{\text{atm}} + P_{\text{(gas stream)}}$

The correction factor I to convert i_m , measured dry-gas meter flow rate, to true flow rate is then

$$I = \frac{F_m}{i_m}$$

The venturi and dry-gas meter were calibrated at three flow rates; 30, 55, and 60 liters/min. Normal system flow rates are 55 to 60 liters/min. The calibration factor for the dry-gas meter is constant at the calibration flows ($\pm 0.2\%$). The average value of flow from seven determinations is used in calculating true flow rates of the system. The plot of venturi ΔP versus flow rate follows a straight line over the range used in calibration. From the slope and intercept of the line flow rates were calculated.

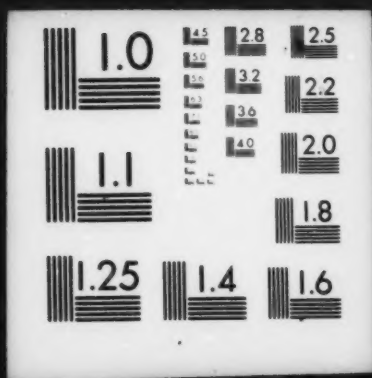
APPENDIX D

WRITTEN COMMUNICATIONS WITH
POTENTIAL COLLABORATORS

20F 2

PB

246843



Dear Sir:

Your name has been given to Midwest Research Institute (MRI) by the Environmental Protection Agency (EPA), as having expressed an interest in becoming a voluntary collaborator in an NO₂ Testing Program, to be sponsored by EPA. I am writing to confirm this expression of interest by your organization.

The objective of this program is to determine the reliability and bias of four methods for measuring NO₂-ambient air. MRI has the responsibilities for organizing the program, furnishing the test facilities, coordinating the testing, analyzing the results of the collaborators, and reporting the findings to EPA.

The sodium-arsenite method--the first method to be evaluated--will be tested in Kansas City, Missouri, during the first part of January 1974. Ten collaborators are needed for each of the four methods. A tentative test schedule of the other three methods is given on the attached "Collaborator Form."

A writeup of the sodium-arsenite method is enclosed, and provides the information needed for a collaborator to perform the testing and analyze the samples he takes.

Each collaborator organization, once chosen, will be reimbursed for travel, subsistence, lodging, and miscellaneous expenses (e.g., shipment of equipment and local travel), for the employee sent to Kansas City to perform the testing. Each collaborator will need to furnish the sampling apparatus called for in the writeup. For each of the two manual methods, sodium-arsenite and TGS-ANSA, six sampling trains will be needed. Cases will be furnished in which to ship field samples to the collaborator's laboratory for analysis.

We would appreciate your completing and returning to us the Collaborator Form before November 15.

Sincerely,

Paul C. Constant, Jr., Head
Environmental Measurements Section

Enclosures: (1) Collaborator Form
(2) Tentative Method for the Determination
of Nitrogen Dioxide in the Atmosphere
(Sodium-Arsenite Method)

COLLABORATOR FORM

1. Methods to Test (Check the ones in which you want to participate as a collaborator):

☐ Sodium Arsenite	☐ TGS-ANSA Procedure
☐ Continuous Saltzman	☐ Chemiluminescent

2. Equipment Available for Test:

Could you furnish six trains for:

Sodium Arsenite: ☐ yes ☐ no

TGS-ANSA: ☐ yes ☐ no

Have you a Colorimetric (Continuous Saltzman) Ambient NO₂ Monitor?

☐ yes ☐ no Make _____ Model _____

Have you a Chemiluminescent Ambient NO₂ Monitor that you would use?

☐ yes ☐ no Make _____ Model _____

3. Test Period (Each Method):

Period acceptable (calendar days):

☐ 6 days ☐ 10 days ☐ 13 days

4. Methods You Have Used:

☐ Sodium Arsenite, ☐ TGS-ANSA, ☐ Continuous Saltzman,
☐ Chemiluminescent, ☐ Others: _____

5. Remarks: _____

6. Company: _____

Address: _____

Person to Contact: _____

Telephone Number: _____



MIDWEST RESEARCH INSTITUTE

425 Volker Boulevard
Kansas City, Missouri 64111
Telephone (816) 561-0200

5 August 1974

Name
Pollution Control Agency
City of Toledo
26 Main Street
Toledo, Ohio 43605

Dear Name:

You have indicated your interest in participating in an EPA-Sponsored NO₂ collaborative test using the Chemiluminescent method. If you desire to be considered as a candidate to participate in this test, would you let me know by 19 August, providing me also with the following information: (1) Whether or not you could provide instrumentation at the test site in Kansas City for your sampling; and (2) If so, the type instrument along with its flow intake rate, and the bench area it will occupy.

We would appreciate your reviewing the enclosed preliminary draft, "Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere (Chemiluminescent Procedure)." After your review, would you use this method to obtain a few sample measurements of your ambient atmosphere and then send me a copy of your results by 26 August. These results will assist us in the selection of ten collaborators.

The 1-week nitrogen dioxide test using the enclosed method is tentatively scheduled to take place in Kansas City, Missouri, with sampling starting on Monday, 23 September. The test will be indoors using a sampling system developed by MRI for this collaborative program. This system, which was used quite successfully for three other methods, is shown in diagram form in the attached figure.

Each collaborator will be reimbursed for travel, subsistence and lodging for the employee it sends to Kansas City to perform this field sampling, as well as for local travel and miscellaneous expenses such as the cost of shipping the instrumentation to be used on site for the sampling. The cost of all materials to be used in the operation of the sampling instruments such as calibration systems, chemicals, etc., are not included and are to be borne by the collaborative organization.

We will be in touch with you as soon as the ten collaborators are selected for this test. If you have any questions, please contact me.

Very truly yours,

Paul C. Constant, Jr., Head
Environmental Measurements Section

PCC:cdn
Enclosures

9 September 1974

This confirms our selection of your organization as one of the 10 collaborators for the EPA-Sponsored Nitrogen Dioxide Collaborative Test Using The Chemiluminescent Method, and presents information about this test.

A copy of the "Tentative Method for the Determination of Nitrogen Dioxide In the Atmosphere (Chemiluminescent Procedure)," dated August 1974, is enclosed for your study and retention. Please destroy any previous write-up we may have given you on the Chemiluminescent Procedure.

The test schedule is given in Table I. The starting date is Monday, 23 September 1974. We will meet in the lobby of the Ramada Inn (See Figure 1, upper right-hand portion) which is located at 87th Street and Highway I-435. From there we will go to the field site which is several miles from the motel. At the site there will be an orientation program of the facilities prior to your preparing your instruments for sampling.

The schedule in Table I is based on the assumptions that all equipment of the collaborators will be on-site early Monday morning, and that all goes well during the week.

The sampling by each collaborator must be performed according to the attached write up.

The sampling system that will be used in this collaborative test is shown in diagram form in Figure 2, an enclosure to this letter. Each collaborator will attach his instrument to ports of the spiked and unspiked manifolds according to a specific experimental design pattern.

There will be two runs per each of four 24-hr periods. The duration of one run will be approximately 14 hr; the other will be 7 hr. For the 14-hr run, all collaborators will sample from the spiked manifold. For the 7-hr runs, each collaborator will sample from each manifold--spiked and unspiked--for approximately 3-1/2 hr.

9 September 1974

The hours 0800-1630 on Monday, 23 September are for collaborator preparation. From then on testing will be according to the following schedule:

<u>Time</u>	<u>Activity</u>	<u>Spiked Line</u>	<u>Unspiked Line</u>
1630-1800	Calibrate	----	----
1800-0800	Sample	1 thru 10	----
0800-0930	Calibrate	----	----
0930-1250	Sample	4, 6, 7, 8, 10	1, 2, 3, 5, 9
1250-1310	Switch Lines	----	----
1310-1630	Sample	1, 2, 3, 5, 9	4, 6, 7, 8, 10

Enclosed is a Teflon adaptor. One of these adaptors constitutes a port of the sampling manifolds. It is the type of port to which you will attach your instrument. The larger-diameter end is the one to which an instrument is to be attached. This adaptor is being sent to you, as an enclosure, so that you will know what size tubing will be required for the connection of your instrument to the sampling manifolds. You will need at least 30 feet of this tubing.

The switching of your instrument between the spiked and unspiked lines will be done manually.

Each collaborator will be reimbursed for travel, subsistence, and lodging for the employee it send to Kansas City to perform the field work as a collaborator, as well as miscellaneous expenses such as costs for shipping the field equipment you will use on site for the sampling. Please keep receipts such as airline tickets and equipment shipment invoices. Mr. Fred Damon, MRI Administrative Officer, will be contacting you to make contractual arrangements. If you have any questions you may contact him at (816) 561-0202.

Reservations will be made by MRI for each collaborator at the Ramada Inn. These lodging charges will be billed directly to MRI, therefore, you will need not consider this expense. Also, if you are not driving to Kansas City, but rather arrive by plane, MRI will provide local transportation.

Upon your arrival at the Kansas City International Airport call Econo-Car-Rent-A-Car Company at 464-5656 and you will be provided a car. As is the case of the motel, these charges will be billed directly to MRI.

If you are not driving and bringing your equipment with you, I suggest that you ship it a couple of weeks before the 23rd of September so that it will be at MRI before 20 September. For your convenience, you could send it to yourself, % Mr. Paul C. Constant, Jr., Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110, COD or prepaid.

Page 3

9 September 1974

To help us with preparations at this end, I would like the following information if you have not already given it to us:

1. The name of the person(s) from your organization who will be coming to Kansas City.
2. The mode of transportation the person will use to come to Kansas City (in case of airline, the airline and flight number), and the time of his arrival.
3. How your equipment will be sent to Kansas City and when it is expected to arrive.

Very truly yours,

Paul C. Constant, Jr., Head
Environmental Measurements Section

PCC:cdn

Enclosures:

1. "Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere."
2. Table I -- Test Schedule
3. Figure 1 -- Map: Ramade Inn to Field Station
4. Map -- Kansas City International Airport to Ramada Inn
5. Map -- Deramus Field Station
6. Figure 2 -- Nitrogen Dioxide Ambient-Air Sampling System Concept
7. Teflon Adaptor

APPENDIX E.

INSTRUCTIONS FOR COLLABORATORS NO₂ COLLABORATIVE

TEST: CHEMILUMINESCENT PROCEDURE

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INSTRUCTIONS FOR COLLABORATORS
NO₂ COLLABORATIVE TEST: CHEMILUMINESCENT PROCEDURE

General Information

1. Calibration, sampling, analysis, etc., should be done explicitly as stated in the August 1974 write-up furnished you on the "Tentative Method for the Determination of Nitrogen Dioxide in the Atmosphere," (Chemiluminescent Procedure).
2. Each collaborator will have an area for his analyzer on one or the other table. Use of connecting tubing to the opposite table will enable alternate sampling of the spiked and unspiked manifolds by each collaborator.
3. For each run, each collaborator will connect his analyzer to either the unspiked manifold or the spiked manifold, according to the instructions given before the run. Heavier tubing, for those collaborators whose instruments require higher flow rates is available in several areas of both the spiked and unspiked side. Please ask the MRI person in charge concerning use of the heavier tubing.
4. Collaborators are urged to make ample explanatory notes on their analyzer charts to coordinate information and aid in data reduction. All pertinent data should appear on the charts.
5. Each collaborator should work independently of other collaborators.
6. On the spiked table, a separate power circuit (120 V 60-cycle, 4-outlet strip) is to be used by each collaborator for his analyzer. On the unspiked side one strip will be shared by two collaborators where necessary. These strips are under the table tops near the periphery of the tops.

Test Instructions

1. Preparation by collaborators will precede sampling runs.
2. Analyzer calibration will be included in preparation time, not to be done during the run.
3. Upon notification of "start testing" from the MRI person on site, collaborators will mark the appropriate place on their analyzer charts. It is expected that the analyzer will be operating and the connecting tubing in proper hook-up arrangement prior to the start signal.

4. Note all pertinent data on the analyzer charts as the run progresses.

5. Upon notification by the MRI person in charge, indicate the end of the run by marking on the analyzer chart.

General Schedule

There will be two runs per each of four 24-hr periods. The duration of one run will be approximately 14 hr; the other will be 7 hr. For the 14-hr runs, all collaborators will sample from the spiked manifold. For the 7-hr runs, each collaborator will sample from each manifold--spiked and unspiked--for approximately $3\frac{1}{2}$ hr.

The hours 0800-1630 on Monday 23 September are for collaborator preparation. From then on testing will be according to the following schedule:

<u>Time</u>	<u>Activity</u>	<u>Spiked Line</u>	<u>Unspiked Line</u>
1630-1800	Calibrate	----	----
1800-0800	Sample	1 thru 10	----
0800-0930	Calibrate	----	----
0930-1250	Sample	4, 6, 7, 8, 10	1, 2, 3, 5, 9
1250-1310	Switch Lines	----	----
1310-1630	Sample	1, 2, 3, 5, 9	4, 6, 7, 8, 10

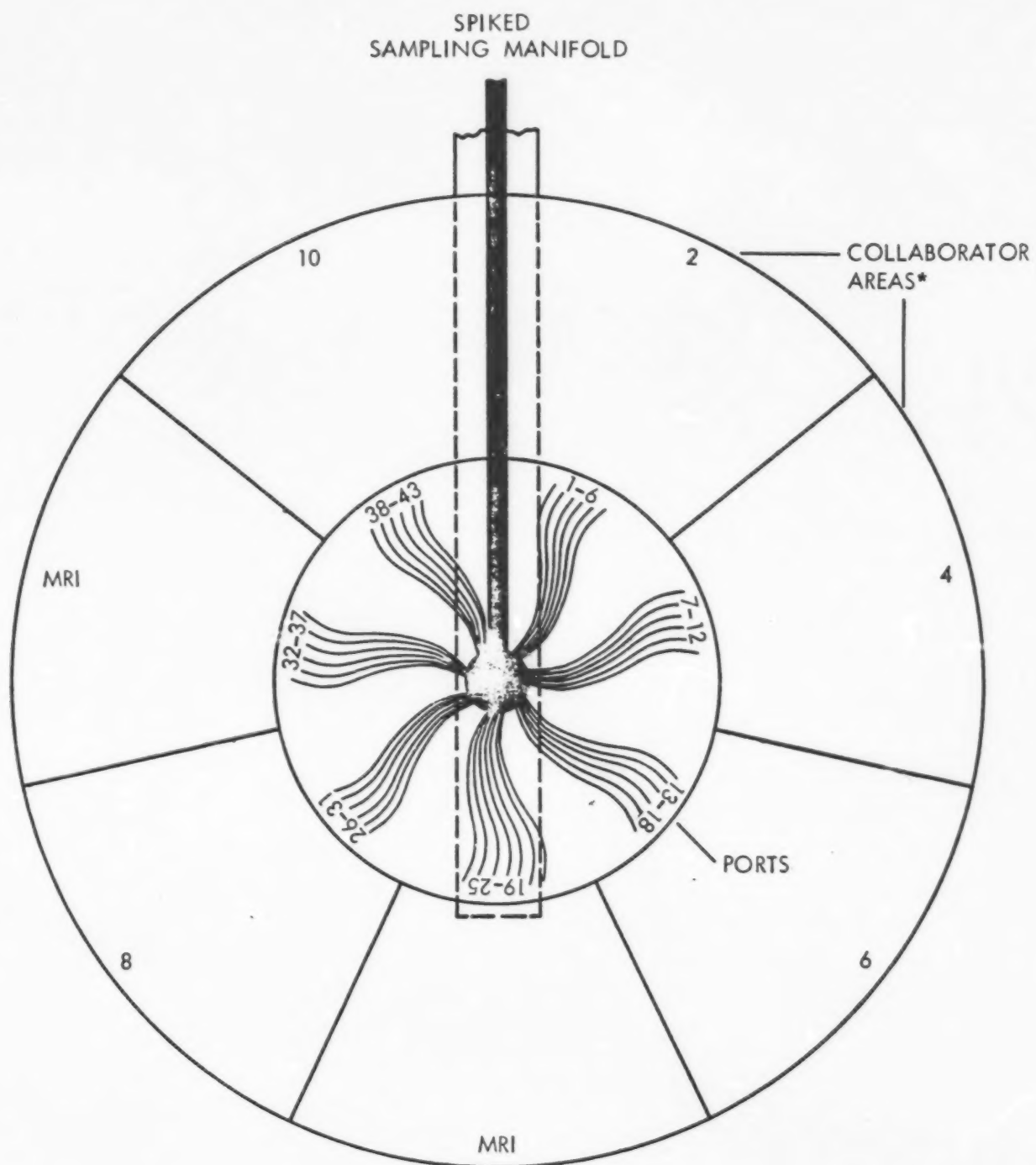
The numbers given in the spiked and unspiked columns are the collaborators' I.D. numbers. (See attached table for your number.)

COLLABORATOR ANALYZER LOCATION AREAS
AND PRINCIPLE PORT ASSIGNMENTS

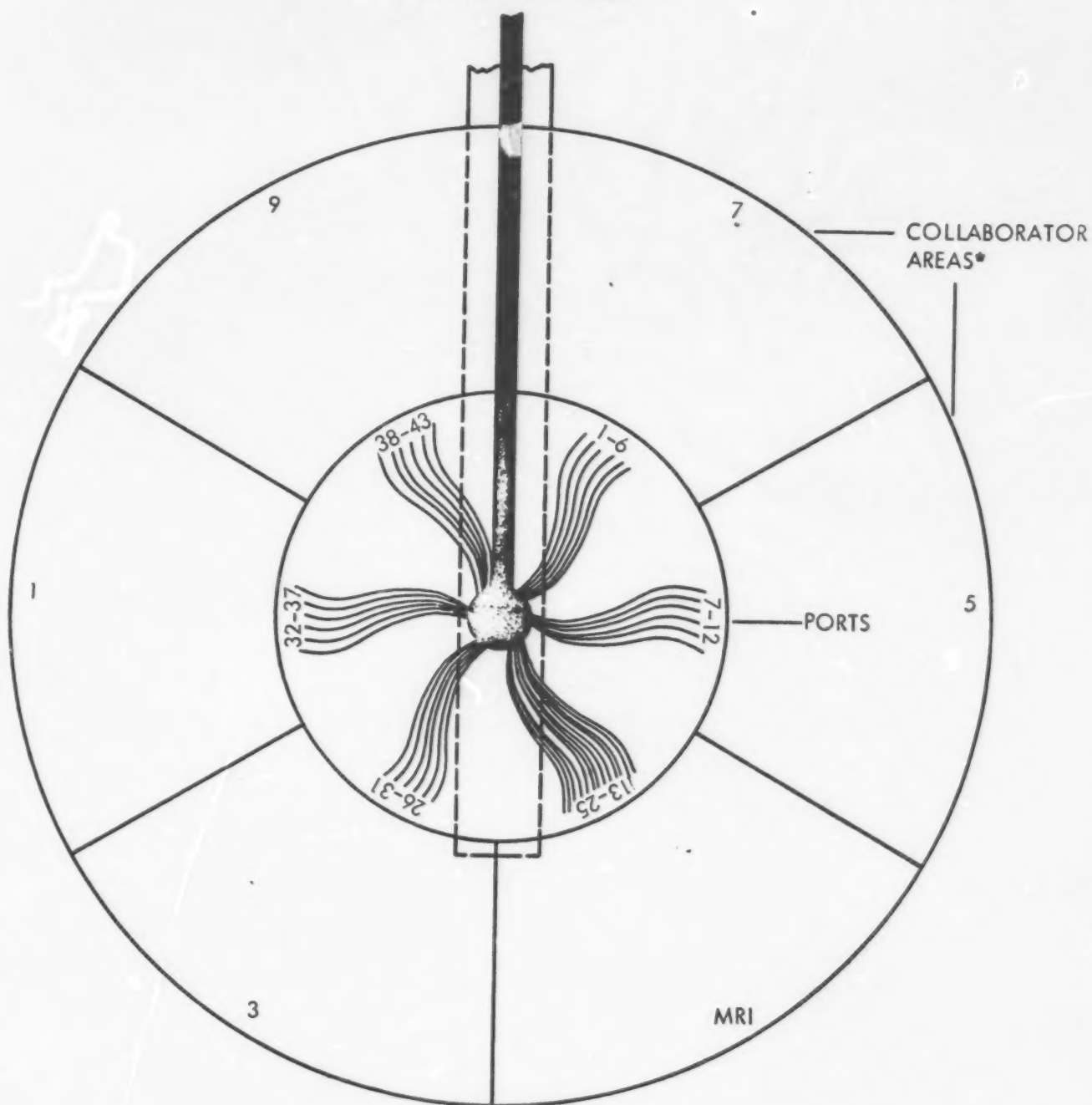
Collaborator		Spiked Table		Unspiked Table	
<u>I.D. No.*</u>	<u>Name</u>	<u>Area</u>	<u>Ports</u>	<u>Area</u>	<u>Ports</u>
	Robert Richardson	--	--	1	32-37
	Jon Zimmer	2	1-6	--	--
	William Findlay	--	--	3	26-31
	Roger Ellard	4	7-12	--	--
	Jim Harris	--	--	5	7-12
	John Higuchi	6	13-18	--	--
	Melvin Ken Muir	--	--	7	1-6
	Carol Ellis	8	26-31	--	--
	Vinson L. Thompson	--	--	9	38-43
	Midwest Research Institute	10	38-43	--	--

NOTE: Assignments of secondary ports (on the opposite table from the analyzer location) will be made prior to the start of each test.

* I.D.'s removed from this report to keep collaborators anonymous.



UNSPIKED
SAMPLING MANIFOLD



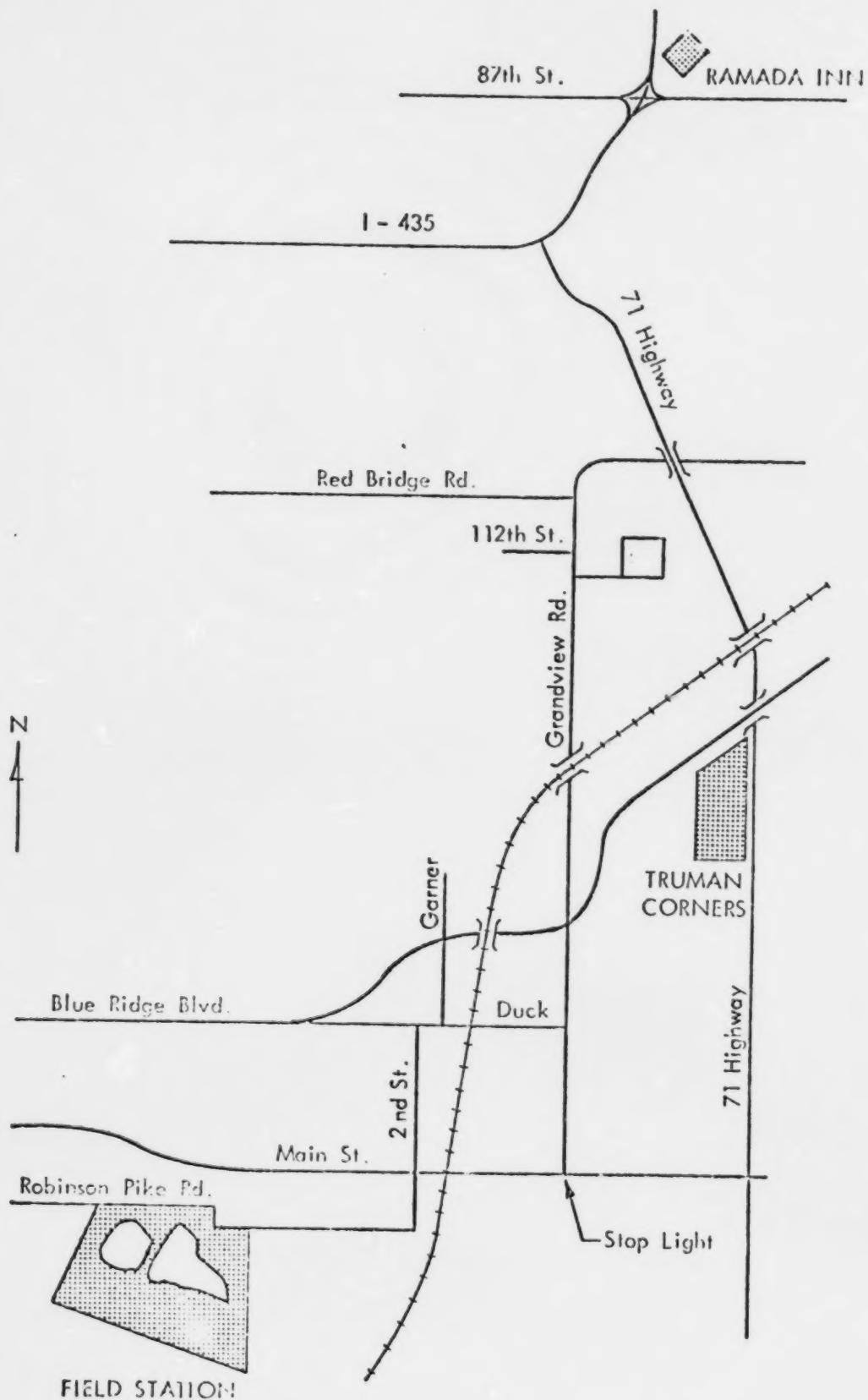
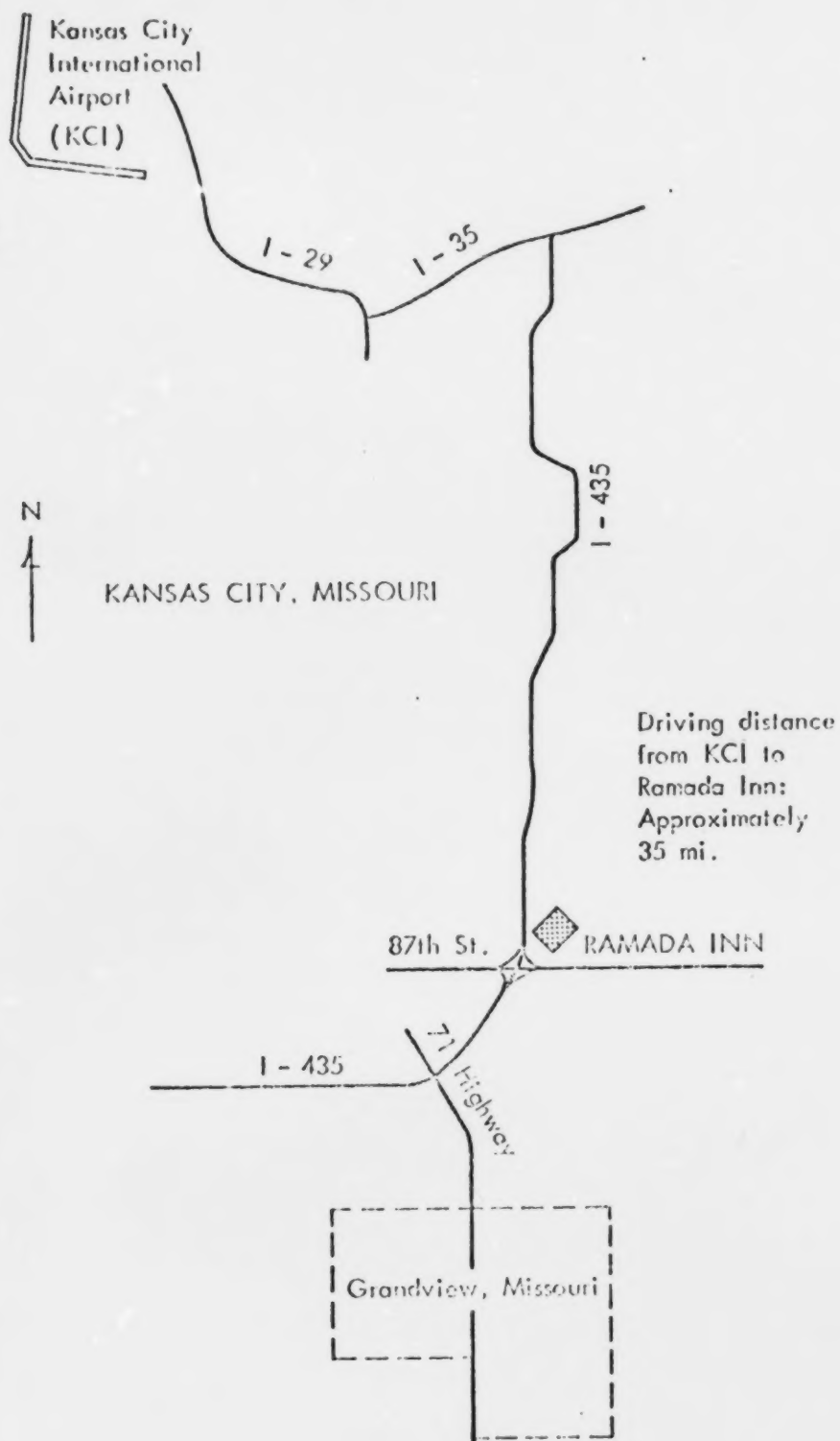
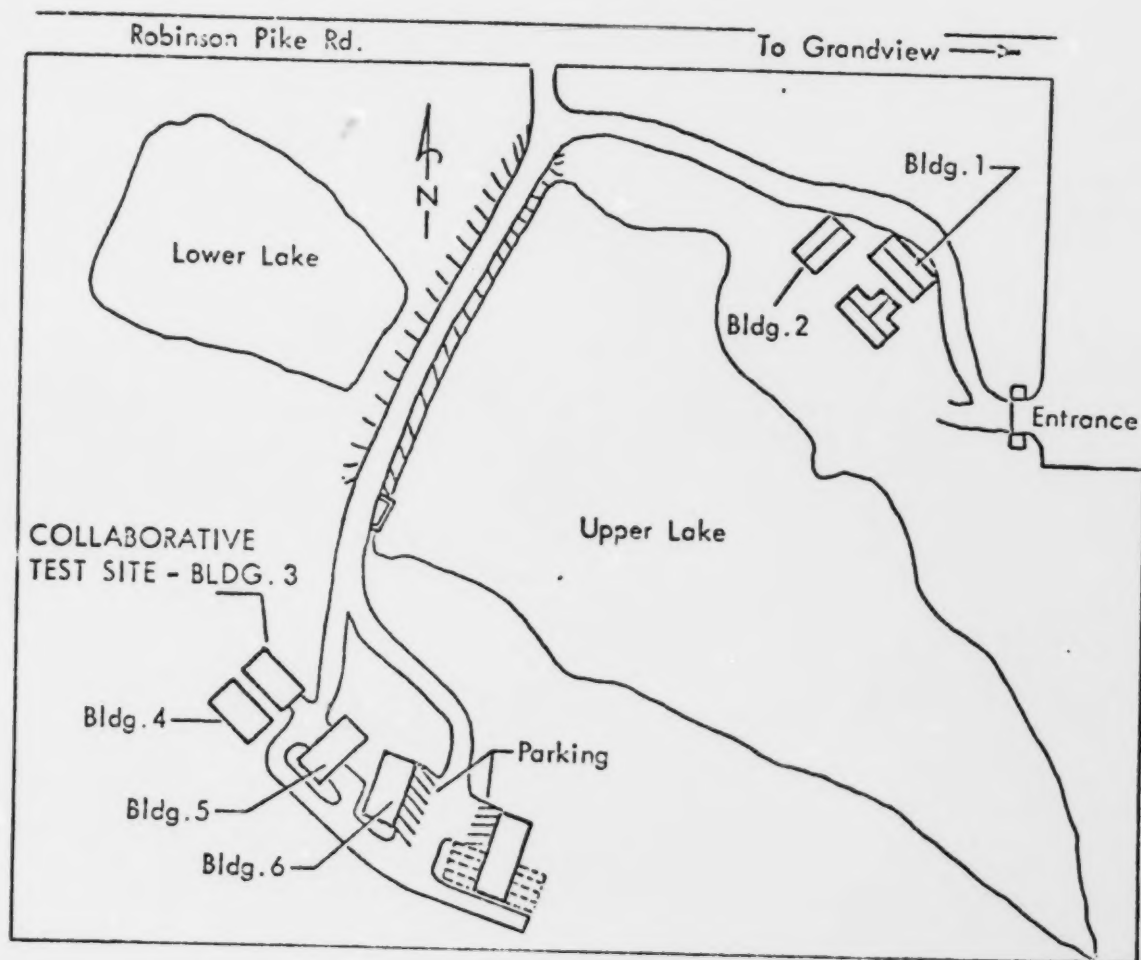


Figure 1 -- Map: Ramada Inn to Field Station



Map -- Kansas City International Airport to Ramada Inn



DERAMUS FIELD STATION
MIDWEST RESEARCH INSTITUTE
GRANDVIEW, MISSOURI

APPENDIX F.

NO₂, SAMPLING SYSTEM DATA: TEST LOG SHEETS

WITH FIELD OPERATIONAL DATA

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Run #1

LOG SHEET

Side 1

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DATE 23 Sep 74																									
TIME								24 Sep 74																	
OUTDOOR TEMP.	1800	1900	2000	2100	2200	2300	2400	0100	0200	0300	0400	0500	0600	0700	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	
WET BULB	64	60	57	55	55	55	55	55	55	54	53	54	55	55	57	60	62	62	67	66	63	58	50	59	
DRY BULB	52	52	51	50	50	50	51	49	51	51	49	49	51	51	53	55	57	57	56	55	56	53	54	53	
REL. HUMIDITY	64%	60	57	55	55	55	55	55	55	54	53	54	55	55	57	60	64	68	65	66	68	58	60	59	
BAR. PRESSURE	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	43.8	
WIND SPEED	1.8	0	0	1.0	1.2	0.8	0	2	1 1/2	0	0	0	0	1	.5	1.5	1.0	4.5	4.2	2.4	5.0	3.6	2.8		
WIND DIRECTION	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	W	W	W	W	S	S		
POWER LIGHTS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
LEAKS PERMEATION ASSEMBLY	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
BATH TEMP.	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	
ROTAMETERS - 2																									
4	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98	97	97	97	96	97	97	
N ₂ PRESSURE	100	95	94	910	900	890	880	860	845	830	810	800	790	780	770	760	750	740	730	720	710	700	690	680	600
RECORDER 1 - PAPER																									
RECORDER 2 - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

LOG SHEET

Side 2

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
TIME	1900	1900	2000	2100	2200	2300	2400	0100	0200	0300	0400	0500	0600	0700	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	
NO ₂ ANALYZER - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
VAC PRESSURE	15	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
O ₂ PRESSURE	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
UNSPIKED - NO	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
NO ₂	2	2	5	7	7	3	3	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
SPIKED - NO	N/A	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
NO ₂	N/A	7	8	9	12	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8	8
VENTURI MANOMETER - HI	532	532	532	534	534	534	536	536	537	537	537	537	537	537	537	537	537	537	537	537	537	537	537	537	537
LO	267	267	267	265	265	265	264	264	263	263	263	263	263	263	263	263	263	263	263	263	263	263	263	263	263
VENTURI ΔP	265	265	265	269	269	269	272	272	274	274	274	274	274	274	274	274	274	274	274	274	274	274	274	274	274
INDOOR TEMP.	25°C	23	23	23	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22
GAS FLOW TEMP.	22°C	22	22	22	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5
GAS FLOW MANOMETER - HI	484	484	484	485	485	485	487	487	487	487	487	487	487	487	487	487	487	487	487	487	487	487	487	487	487
LO	370	370	370	369	369	369	370	370	370	370	370	370	370	370	370	370	370	370	370	370	370	370	370	370	370
GAS FLOW PRESSURE	114	114	114	116	116	116	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117
EXHAUST - U MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
S MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
CHECK SAMPLE TRAINS	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
INITIALS	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE	DE
meter flow rate (pressure) 2 mci.	58.5	58.1	58.2	58.0	57.6		56	57	57.3	57.6	57.1	57.4	57.6	57.9	58.2	58.7	58.7	58.7	58.7	58.7	58.7	58.7	58.7	58.7	58.7

Chemiluminescence
Run #2

LOG SHEET

Side 1

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DATE																									
TIME																									
OUTDOOR TEMP.	1800	1900	2000	2100	2200	2300	2400	0100	0200	0300	0400	0500	0600	0700	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	
WET BULB	57	57	55	55	55	56	56	55	54	53	53	52	52	52	52	52	52	52	52	52	52	52	52	52	
DRY BULB	53	53	52	52	52	53	52	52	51	51	51	50	50	50	50	50	50	50	50	50	50	50	50	50	
REL. HUMIDITY	57	57	55	55	55	56	55	55	54	53	53	52	52	52	52	52	52	52	52	52	52	52	52	52	
BAR. PRESSURE	77	77	82	82	82	82	82	82	82	87	87	87	87	87	87	87	87	87	87	87	87	87	87	87	
WIND SPEED	741	741	741	741	741	741	741	741	741	741	741	741	741	741	741	741	741	741	741	741	741	741	741	741	
WIND DIRECTION	3.0	1.8	2.2	0	2.2	0.8	1.2	0	1	1	2	0	0	0	0	0	0	0	0	0	0	0	0	0	
POWER LIGHTS	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	5	
LEAKS PERMEATION ASSEMBLY	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
BATH TEMP.	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	
ROTAMETERS - 1	100	100	99	99	99	99	99	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	
2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
3	100	100	99	99	99	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	
4	98	97	97	96	97	98	96	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98	98	
N ₂ PRESSURE	575	550	540	535	500	500	500	490	460	450	440	430	420	400	350	340	320	300	300	300	270	250	185	185	
RECORDER 1 - PAPER																									
OPERATION																									
RECORDER 2 - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	

LOG SHEET

Side 2

24 25 SEP

TIME	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
NO ₂ ANALYZER - PAPER	1800	1900	2000	2100	2200	2300	2400	0100	0200	0300	0400	0500	0600	0700	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
VAC PRESSURE	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	
O ₂ PRESSURE	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	
UNSPIKED - NO	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	
NO ₂	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	
SPIKED - NO	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	
NO ₂	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	
VENTURI MANOMETER - HI	535	535	535	535	535	535	535	535	535	535	535	535	535	535	535	535	535	535	535	535	535	535	535	535	
LO	263	263	263	263	263	263	263	263	263	263	263	263	263	263	263	263	263	263	263	263	263	263	263	263	
VENTURI ΔP	272	272	272	272	272	272	272	272	272	272	272	272	272	272	272	272	272	272	272	272	272	272	272	272	
INDOOR TEMP.	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	
GAS FLOW TEMP.	21.5	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	
GAS FLOW MANOMETER - HI	485	485	485	485	485	485	485	485	485	485	485	485	485	485	485	485	485	485	485	485	485	485	485	485	
LO	368	368	368	368	368	368	368	368	368	368	368	368	368	368	368	368	368	368	368	368	368	368	368	368	
GAS FLOW PRESSURE	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	117	
EXHAUST - U MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
S MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
CHECK SAMPLE TRAINS	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
INITIALS	DB	DB	DB	DB	DB	DB	DB	DB	DB	DB	DB	DB	DB	DB	DB	DB	DB	DB	DB	DB	DB	DB	DB	DB	
sec./200 ³	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	57.5	

Chemiluminescence
Run #3

LOG SHEET

Side 1

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DATE																									
TIME																									
OUTDOOR TEMP.	1800	1900	2000	2100	2200	2300	2400	0100	0200	0300	0400	0500	0600	0700	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	
WET BULB	75	75	73	64	63	62	61	61	58	58	57	57	56	56	54	54	62	66	70	74	75	79	79	77	
WET BULB	59	59	57	56	57	59	54	52	57	57	56	54	55	55	54	54	53	62	63	66	66	66	66	65	
WET BULB	75	75	73	64	63	62	61	61	58	58	57	57	56	56	54	54	62	66	70	74	75	79	79	77	
REL. HUMIDITY	37	37	35	60	69	84	87	67	89	89	94	94	94	94	94	94	84	80	68	65	62	50	50	52	
BAR. PRESSURE	737	737	737	736	736	736	736	736	736	736	736	736	736	736	736	736	736	736	736	736	736	736	736	736	
WIND SPEED	0	0	0	0	0	0	0	2	1 1/2	2	2	2	1	0	1	1	1	1	2	2	2	2	2	2	
WIND DIRECTION	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	
POWER LIGHTS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
LEAKS PERMEATION ASSEMBLY	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
BATH TEMP.	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	
ROTAMETERS - 1	97	97	96	96	96	96	96	96	96	96	96	96	96	96	96	96	96	96	96	96	96	96	96	96	
2	95	94	94	94	94	94	94	94	94	94	94	94	94	94	94	94	94	94	94	94	94	94	94	94	
3	98	97	97	97	97	97	97	97	97	97	97	97	97	97	97	97	97	97	97	97	97	97	97	97	
4	96	95	94	94	95	94	94	94	94	94	94	94	94	94	94	94	94	94	94	94	94	94	94	94	
N ₂ PRESSURE	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	2K	
RECORDER 1 - PAPER	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
OPERATION	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
RECORDER 2 - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	

LOG SHEET

Side 2

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
TIME	1900	1900	2000	2100	2200	2300	2400	0100	0200	0300	0400	0500	0600	0700	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	
NO ₂ ANALYZER - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
VAC PRESSURE	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
O ₂ PRESSURE	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
UNSPIKED - NO	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
NO ₂	2	2	2	3.5	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
SPIKED - NO	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
NO ₂	32	31.5	32	33	33	33	31	31	31	31	31	31	31	31	31	31	32	32	32	31.5	31.5	31	31	31	31
VENTURI MANOMETER - HI	530	530	527	527	530	530	530	530	534	533	533	533	531	531	530	529	529	527	527	528	527	527	527	527	527
LO	266	266	269	269	266	266	266	266	266	264	264	264	264	264	264	267	267	267	267	267	267	267	267	267	267
VENTURI ΔP	264	264	259	258	264	264	264	264	271	269	269	269	269	265	265	263	262	262	259	258	259	257	262	258	258
INDOOR TEMP.	23	23	23	23	23	23	23	23	23	22	22	22	22	22	22	22	23	22	22	22	22	23	23	23	23
GAS FLOW TEMP.	23	23	22.5	22	22	22	22	22	22	22	22	22	22	22	22	21.5	21.5	21.5	22.5	22.5	22	22	22	22	22
GAS FLOW MANOMETER - HI	483	483	483	483	483	483	484	484	485	485	485	485	485	483	483	483	483	483	483	482	482	482	482	482	482
LO	368	368	368	368	368	368	368	368	368	368	368	368	368	368	368	367	367	367	367	367	367	367	367	367	367
GAS FLOW PRESSURE	115	115	115	115	115	115	115	115	117	117	117	117	117	113	113	114	114	114	113	113	113	113	113	113	113
EXHAUST - U MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
S MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
CHECK SAMPLE TRAINS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
INITIALS	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500	500

CHEMILUMINESCENCE

Run # 4

LOG SHEET

Side 1

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
DATE																									
TIME																									
OUTDOOR TEMP.	1900	1900	2000	2100	2200	2300	2400	0100	0200	0300	0400	0500	0600	0700	0800	0900	1000	1100	1200	1300	1400	1500	1600	1700	1800
WET BULB	75	74	68	66	65	63	62	62	60	59	59	58	58	58	62	63	65	65	69	70	74	75	76	76	76
DRY BULB	65	64	62	61	61	60	60	60	58	57	57	57	57	57	58	60	61	60	62	63	65	65	66	66	66
REL. HUMIDITY	75	74	68	66	65	63	62	62	60	59	59	58	58	58	62	63	65	65	69	70	74	75	76	76	76
BAR. PRESSURE	58	58	71	75	80	84	89	89	89	89	89	94	94	94	84	84	80	75	67	68	61	58	59	59	59
WIND SPEED	729	729	729	729	729	729	729	729	729	728	728	728	728	728	728	728	728	728	728	728	727	727	727	727	727
WIND DIRECTION	2.2	4.0	1.2	1.2	2.0	2.2	1.5	1.0	0	1	2	2	0	1	4	2.0	2.6	4.0	3.5	3.8	2.9	1.2	2	2	2
POWER LIGHTS	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S	S
LEAKS PERMEATION ASSEMBLY	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
BATH TEMP.	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1	25.1
ROTAMETERS - 1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3	102	102	102	102	102	102	102	102	102	102	102	102	102	102	102	102	102	102	102	102	102	102	102	102	102
4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
N ₂ PRESSURE	1750	1700	1650	1600	1550	1500	1450	1400	1350	1300	1250	1200	1150	1100	1050	1000	950	900	850	800	750	700	650	600	550
RECORDER 1 - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
RECORDER 2 - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓

LOG SHEET

Side 2

TIME	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
NO ₂ ANALYZER - PAPER	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
OPERATION	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
VAC PRESSURE	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25	25
O ₂ PRESSURE	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20	20
UNSPIKED - NO	3	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
NO ₂	2	4	3	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
SPIKED - NO	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
NO ₂	12	12	14	13	13	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12
VENTURI MANOMETER - HI	527	527	527	527	527	527	527	527	527	527	527	527	527	527	527	527	527	527	527	527	527	527	527	527	527
LO	168	268	268	268	267	267	267	267	267	267	267	267	267	267	267	267	267	267	267	267	267	267	267	267	267
VENTURI ΔP	259	259	255	259	261	261	261	262	262	262	262	262	262	262	262	262	262	262	262	262	262	262	262	262	262
INDOOR TEMP.	23	23	23	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22
GAS FLOW TEMP.	22.5	22.5	22.5	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22
GAS FLOW MANOMETER - HI	481	481	481	481	481	481	483	483	483	483	483	483	483	483	483	483	483	483	483	483	483	483	483	483	483
LO	370	370	370	370	370	370	370	370	370	370	370	370	370	370	370	370	370	370	370	370	370	370	370	370	370
GAS FLOW PRESSURE	111	111	111	111	111	111	115	115	115	115	113	113	113	113	113	113	113	113	113	113	113	113	113	113	113
EXHAUST - U MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
S MANIFOLD	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
CHECK SAMPLE TRAINS	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
INITIALS	52.6	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5	52.5

APPENDIX G

FIELD DATA

The first eight columns of Tables G-1 through G-4 list various readings used in calculating flow rates and spike levels, which are given in columns 9 through 13. The last six columns list various ambient-air conditions at the test site. The venturi and meter flow rates (columns 9 and 10) are calculated from the calibration equations in Appendix C. Due to the temperature compensation of the dry-gas meter and the above-ambient pressure of the gas stream at these instruments, the flow rates are calculated at 21°C and 760 mm Hg. The readings of the two devices are then averaged (column 11) and the sampling ports (column 12). Some of the methods being evaluated with this system are not corrected for temperature and pressure. However, if the spike levels are not calculated at the temperature and pressure existing at the manifold ports, a significant degree of uncertainty enters into any subsequent use of the spike level. The spike level (column 13) is determined from the permeation rates of the permeation tubes used in each test.

Table G-1. LEVEL 1 TEST DATA

No. Sampling System Data										Calculated Flowrates and Spike Levels										Ambient Conditions				
Date Time	Bar. Press. (mm Hg)	Flow Temp. (°C)	Flow Rate (L/min)	Venturi Pressure Reading (mm H ₂ O)	N ₂ Carrier Flowrate (cc/min)	Permeation Tube Temp. (°C)	Flowrate			Average Flowrate			Spike Level Ambient/ DUV(m ³)		No. Back- ground (µg/m ³)	No. Back- ground (µg/m ³)	Dut- door Temp. (°C)	Wind Speed (m/sec)	Wind Direc- tion	Relative Humidity (%)				
							Venturi to 21" + 760 mm Hg (L/min)	Meter to 21" + 760 mm Hg (L/min)	Meter to 21" + 760 mm Hg (L/min)	Average Flowrate to 21" + 760 mm Hg (L/min)	Average Flowrate to 21" + 760 mm Hg (L/min)	Average Flowrate to 21" + 760 mm Hg (L/min)	Spike Level Ambient/ DUV(m ³)											
9-23-76																								
1800	744	8	32.0	58.1	265	200	25.1	59.4	58.7	58.7	59.0	60.5	60.5	49.0	0	0	64	5	S	43				
1900	743	8	22.0	58.4	265	200	25.1	59.3	58.9	58.9	59.1	60.7	60.7	49.0	0	0	60	0	S	58				
2000	743	8	22.0	58.4	265	200	25.1	59.3	58.9	58.9	59.1	60.7	60.7	49.0	0	0	57	0	S	66				
2100	743	8	22.0	58.6	269	200	25.1	59.8	59.1	59.1	59.5	61.0	61.0	48.7	0	0	55	3	S	70				
2200	743	8	21.5	59.0	269	200	25.1	59.9	59.5	59.5	59.7	61.2	61.2	48.6	0	0	55	4	S	70				
2300	744	8	21.5	-	269	200	25.1	59.9	-	-	59.9	61.3	61.3	48.5	0	0	55	3	S	70				
2400	744	8	21.5	60.7	272	200	25.1	60.3	61.3	61.3	60.8	62.2	62.2	47.7	0	0	55	0	S	76				
9-24-76																								
0100	744	8	21.5	59.6	272	200	25.1	60.3	60.2	60.2	60.3	61.7	61.7	48.2	0	0	55	5	S	65				
0200	744	8	21.5	59.3	274	200	25.1	60.6	59.9	59.9	60.2	61.6	61.6	48.2	0	0	55	4	S	70				
0300	744	8	21.5	59.0	272	200	25.1	60.3	59.6	59.6	60.0	61.4	61.4	48.4	0	0	54	0	S	81				
0400	744	8	22.0	59.2	274	200	25.1	60.7	59.8	59.8	60.2	61.5	61.5	48.3	0	0	53	0	S	75				
0500	744	8	22.0	59.0	274	200	25.1	60.5	59.8	59.8	60.1	61.6	61.6	48.2	0	0	54	0	S	65				
0600	744	8	22.0	59.0	274	200	25.1	60.5	59.6	59.6	60.0	61.5	61.5	48.3	0	0	55	0	S	76				
0700	744	8	21.5	58.4	267	200	25.1	59.6	58.9	58.9	59.3	60.7	60.7	48.9	0	0	57	2	S	77				
0800	743	8	22.0	58.4	265	200	25.1	59.2	58.9	58.9	59.0	60.7	60.7	48.9	0	0	60	4	S	73				
0900	742	8	22.0	57.9	262	200	25.1	58.8	58.4	58.4	58.6	60.2	60.2	49.3	0	0	62	3	M	65				
1000	740	8	22.0	58.4	269	200	25.1	59.5	58.7	58.7	59.1	60.9	60.9	48.8	0	0	62	11	M	50				
1100	742	8	22.0	58.6	270	200	25.1	59.8	59.1	59.1	59.4	61.1	61.1	48.6	0	0	67	10	M	56				
1200	742	8	22.0	58.4	267	200	25.1	59.4	58.9	58.9	59.2	60.8	60.8	48.9	0	0	66	6	M	64				
1300	742	8	22.0	58.8	271	200	25.1	59.5	59.3	59.3	59.6	61.2	61.2	48.5	0	0	63	12	M	64				
1400	742	8	22.5	59.0	271	200	25.1	59.8	59.5	59.5	59.6	61.4	61.4	48.4	0	5	58	9	S	72				
1500	742	8	22.0	58.9	271	200	25.1	59.8	59.4	59.4	59.6	61.3	61.3	48.5	0	0	60	7	S	68				
1600	741	8	22.0	59.0	271	200	25.1	59.8	59.4	59.4	59.6	61.4	61.4	48.4	10	0	59	-	S	67				

a/ Temperature and pressure at sampling ports.

Table G-2. LEVEL 2 TEST DATA

NO ₂ Sampling System Data										Calculated Flowrates and Spike Levels									
Date	Bar. Press. (mm Hg)	Flow Press. (mm Hg)	Flow Temp. (°C)	Flow Meter (L/min)	Venturi Rate Meter (mm H ₂ O)	Venturi Pressure Reading (mm H ₂ O)	N ₂ Carrier Flowrate (cc/min)	Formation Tube Temp. (°C)	Venturi to 21" + 760 mm Hg (L/min)	Meter to 21" + 760 mm Hg (L/min)	Average Flowrate to 21" + 760 mm Hg (L/min)	Spike Level Ambient g/(m ³)	NO Back-ground (µg/m ³)	NO ₂ Back-ground (µg/m ³)	Ambient Conditions	Wind Speed (m/sec)	Wind Direction	Relative Humidity (%)	
9-24-74																			
1800	741	8	21.5	59.1	272		600	25.1	60.1	59.5	59.8	61.4	186	-	-	57	7	S	77
1900	741	8	22.0	59.1	272		600	25.1	60.0	59.5	59.7	61.5	185	0	0	57	5	S	77
2000	741	8	22.0	59.0	272		600	25.1	60.0	59.4	59.7	61.4	186	0	0	55	6	S	82
2100	741	8	21.5	59.0	272		600	25.1	60.1	59.4	59.7	61.4	186	0	0	55	0	S	82
2200	741	8	21.5	59.5	272		600	25.0	60.2	60.0	60.1	61.6	185	0	0	55	6	S	82
2300	741	8	21.0	59.4	272		600	25.0	60.2	60.0	60.1	61.6	185	0	0	56	3	S	82
2400	741	8	21.0	59.6	272		600	25.0	60.2	60.0	60.1	61.6	185	0	0	55	4	S	82
9-25-74																			
0100	741	8	21.0	59.5	272		600	25.0	60.2	59.9	60.0	61.6	185	0	0	55	0	S	82
0200	741	8	21.5	59.6	277		600	25.0	60.7	60.0	60.3	62.0	184	0	0	54	3	S	82
0300	741	8	21.0	59.6	277		600	25.0	60.8	60.0	60.4	61.9	184	0	0	53	5	S	87
0400	741	8	21.0	59.7	277		600	25.0	60.8	60.1	60.4	62.0	184	0	0	53	3	S	87
0500	741	8	21.0	59.7	277		600	25.0	60.8	60.1	60.4	62.0	184	0	0	52	0	S	87
0600	741	8	21.0	59.6	275		600	25.0	60.5	60.2	60.4	61.9	184	0	0	52	0	S	87
0700	741	8	21.0	59.6	275		600	25.0	60.5	60.0	60.3	61.8	184	0	0	52	0	S	87
0800	740	8	21.0	57.7	269		600	25.0	59.7	58.0	58.9	60.5	186	0	0	52	0	S	87
0900	740	8	22.0	57.5	266		600	25.1	59.2	57.8	58.9	60.5	186	0	0	58	4	W	83
1000	740	8	22.5	58.2	285		600	25.1	58.9	58.5	58.7	60.3	189	0	0	57	1	W	84
1100	740	8	23.0	58.1	282		600	25.1	58.5	58.4	58.7	60.6	188	5	10	63	1	W	84
1200	740	8	23.0	59.1	272		600	25.1	59.7	59.4	59.5	61.6	185	5	20	67	1	W	62
1300	740	8	23.0	58.6	269		600	25.1	59.3	58.9	59.1	61.5	185	5	15	72	0	W	53
1400	739	8	23.0	58.4	267		600	25.1	59.0	58.6	58.8	60.3	186	5	5	75	1	W	44
1500	738	8	23.0	58.4	264		600	25.1	58.6	58.6	58.6	60.7	187	5	0	77	0	W	36
1600	738	8	23.0	58.5	264		600	25.1	58.6	58.7	58.6	60.7	188	0	5	78	0	W	27
1700	737	8	23.0	58.1	264		600	25.1	58.5	58.2	58.3	60.8	187	5	0	75	6	W	51
											58.3	60.8	188	-	-	75	0	W	54
														1	3				

Table G-1. LEVEL 1 TEST DATA

N ₂ Sampling System Data										Flowrates and Spike Levels				Ambient Conditions			
Bar. Press. (mm Hg)	Flow Temp. Meter (°C)	Flow Rate Meter (L/min)	Venturi Pressure Reading (mm H ₂ O)	N ₂ Carrier Flowrate (cc/min)	Permeation Tube Temp. (°C)	Venturi to 210 + 760 mm Hg (L/min)	Water to 210 + 760 mm Hg (L/min)	Average Flowrate + 760 mm Hg (L/min)	Spike Level Ambient (L/min)	Back-ground (L/min)	Back-ground (L/min)	Out-door Temp. (°C)	Wind Speed (m/sec)	Wind Direction	Relative Humidity (%)		
9-25-74																	
737	8	23.0	58.1	264	800	25.1	58.5	58.2	58.3	0	0	75	0	S	37		
1800	737	8	23.0	58.1	264	800	25.1	58.5	58.3	0	0	75	0	S	37		
1900	737	8	23.0	58.1	264	800	25.1	58.5	58.3	0	0	75	0	S	37		
2000	737	8	22.5	57.7	258	800	25.1	57.9	57.8	0	0	73	0	S	35		
2100	736	8	22.0	57.9	258	800	25.1	57.9	57.9	0	15	64	0	S	60		
2200	736	8	22.0	58.2	264	800	25.1	58.2	58.4	0	0	63	0	S	69		
2300	736	8	22.0	58.3	264	800	25.1	58.6	58.3	0	0	62	0	S	64		
2400	736	8	22.0	58.4	264	800	25.1	58.6	58.5	0	0	61	0	S	89		
9-26-74																	
736	8	22.0	58.8	266	800	25.1	58.6	58.8	58.7	0	0	61	5	S	67		
0100	736	8	22.0	58.8	271	800	25.1	59.4	59.1	0	0	58	4	S	89		
0200	736	8	22.0	58.7	269	800	25.1	59.2	59.0	0	0	58	5	S	89		
0300	736	8	22.0	59.2	269	800	25.1	59.2	58.9	0	0	57	5	S	94		
0400	736	8	22.0	59.1	269	800	25.1	59.2	59.2	0	0	57	3	S	94		
0500	736	8	22.0	58.5	265	800	25.1	58.7	58.6	0	0	56	0	S	94		
0600	736	8	22.0	58.6	265	800	25.1	58.7	58.6	0	0	56	3	S	94		
0700	736	8	21.5	58.1	263	800	25.1	58.4	58.6	0	0	59	0	S	94		
0800	734	8	21.5	58.1	262	800	25.1	58.3	58.1	0	0	62	3	M	100		
0900	734	8	21.5	58.1	262	800	25.1	58.3	58.1	0	0	62	3	M	84		
1000	734	8	21.5	58.1	262	800	25.1	58.3	58.1	0	0	66	4	M	80		
1100	730	8	22.0	57.9	259	800	25.1	57.5	57.5	0	0	70	6	M	68		
1200	733	8	22.5	58.0	258	800	25.1	57.5	57.7	0	0	74	4	S	65		
1300	732	8	22.0	58.1	259	800	25.1	57.7	57.7	0	10	75	5	S	62		
1400	731	8	22.0	58.2	257	800	25.1	57.4	57.6	0	0	79	6	S	50		
1500	730	8	22.5	58.0	262	800	25.1	57.8	57.5	0	0	79	5	S	50		
1600	730	8	23.0	58.1	258	800	25.1	57.2	57.4	0	0	77	6	S	52		
1700	730	8	23.0	58.1	258	800	25.1	57.2	57.4	1	1						

a/ Temperature and pressure at sampling ports.

Table G-4. LEVEL 4 TEST DATA

W02 Sampling System Data										Calculated Flowrates and Spike Levels				Ambient Conditions			
Date	Time	Bar. Press. (mm Hg)	Flow Temp. (°C)	Flow rate (L/min)	Venturi Pressure Reading (mm H2O)	N2 Carrier Flowrate (cc/min)	Permeation Tube Temp. (°C)	Venturi to 21° + 760 mm Hg (L/min)	Water to 21° + 760 mm Hg (L/min)	Average Flowrate to 21° + 760 mm Hg (L/min)	Spike Level Ambient (µg/m³)	W02 back-around (µg/m³)	W02 back-around (µg/m³)	Out-door Temp. (°C)	Wind Speed (m/sec)	Wind Direction	Relative Humidity (%)
9-26-74																	
1800		729	8	22.5	58.0	259	25.1	57.4	57.4	57.4	53.0b/	10	0	75	6	S	58
1900		729	8	22.5	58.1	259	25.1	57.4	57.5	57.4	102	0	20	74	5	S	58
2000		729	8	22.5	58.1	255	25.1	56.9	57.5	57.2	102	0	10	68	4	S	71
2100		729	8	22.0	58.0	259	25.1	57.4	57.4	57.4	102	0	0	66	4	S	75
2200		729	8	22.0	58.2	261	25.1	57.7	57.6	57.7	102	0	0	65	5	S	80
2300		729	8	22.0	58.5	261	25.1	57.7	57.9	57.8	102	0	0	63	6	S	76
2400		729	8	22.0	58.5	261	25.1	57.7	57.9	57.8	102	0	0	62	4	S	89
9-27-74																	
0100		729	8	22.0	58.6	262	25.1	57.8	58.0	57.9	101	0	0	62	3	S	89
0200		729	8	22.0	58.8	262	25.1	57.8	58.2	58.0	101	0	0	60	0	S	89
0300		728	8	22.0	58.5	262	25.1	57.7	57.9	57.8	101	0	0	59	3	S	89
0400		728	8	22.0	58.5	264	25.1	58.0	57.9	57.9	101	0	10	59	5	S	89
0500		728	8	22.0	58.6	264	25.1	58.0	58.0	58.0	101	0	10	58	5	S	94
0600		728	8	22.0	58.5	264	25.1	58.0	57.9	57.9	101	0	0	58	0	S	94
0700		728	8	22.0	58.7	260	25.1	57.5	58.1	57.8	103	0	0	58	3	S	94
0800		728	8	22.0	57.7	258	25.1	57.7	57.2	57.2	103	0	0	62	2	M	84
0900		728	8	21.5	58.0	237	25.1	57.2	57.1	57.2	103	0	0	63	5	M	84
1000		728	8	21.5	57.7	237	25.1	57.2	57.1	57.2	102	0	0	65	7	M	84
1100		728	8	22.0	57.5	235	25.1	56.9	56.9	56.9	103	0	20	65	10	S	75
1200		728	8	22.5	57.7	235	25.1	56.8	57.1	56.9	103	0	5	69	8	S	67
1300		728	8	22.5	57.3	233	25.1	56.6	56.7	56.6	103	0	5	70	9	SE	68
1400		727	8	22.5	58.0	239	25.1	57.2	57.3	57.2	102	0	5	74	7	SE	61
1500		727	8	22.5	58.1	239	25.1	57.2	57.4	57.3	102	0	5	80	4	SE	58
1600		727	8	22.5	58.1	236	25.1	57.1	57.4	57.2	102	0	5	76	5	SE	59
1630		727	8	22.5	57.9	238	25.1	57.1	57.2	57.1	102	0	5	76	5	SE	59

a/ Temperature and pressure at sampling ports.
b/ Initial spike level incorrect--changed to proper level at 1820.